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THE

CHEMICAL GAZETTE,

OR,

JOURNAL OF PRACTICAL CHEMISTRY,

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS AND MANUFACTURES.

CONDUCTED BY

WILLIAM FRANCIS, PH.D., F.L.S., F.R.A.S., F.C.S.

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THE

CHEMICAL GAZETTE.

No. CCXXI.—January 1, 1852.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Polymeric Isomorphism of Organic Bodies.

By Dr. RUDOLPH WAGNER.

SCHEERER'S hypothesis of polymeric isomorphism has recently been the subject of much controversy among chemists. All that has been written, either on the one side or the other, refers exclusively to inorganic bodies; and if the existence of this kind of isomorphism has not been fully proved to obtain among them, there is strong evidence in favour of that opinion. But whatever is true of inorganic bodies must also be true of organic; and upon this principle the author attempts to apply the hypothesis of polymeric isomorphism to the latter class of compounds.

Scheerer illustrates the theory of isomorphism by comparing a chemical compound to a building, the form of which does not depend upon the kind of material, but upon the size and shape of the individual stones. A piece of a wall may consist of four stones of equal size, for example sandstone; if one stone is taken out, and the hole filled with another, say a brick, the contour of the whole will not have been changed. Just in the same way a constituent may be extracted from a crystallized body, and replaced by another, without alteration of the original crystalline form. The simplest kind of isomorphism is when the replacement of a constituent by another takes place atom for atom; this is called, in opposition to the polymeric, the monomeric isomorphism.

In the case of a piece of wall, however, any one of the stones may be replaced by n stones, and n stones of one kind may be replaced by m stones of another kind, the contour remaining the same throughout. When in a compound crystalline body one constituent atom is replaced by several atoms of another body without alteration of the crystalline form, the isomorphism is then called polymeric, or isomorphism of bodies having different atomic constitution. The existence of a polymeric isomorphism was suspected by several chemists before Scheerer. Thus in Otto's edition of Graham's 'Elements of Chemistry,' 1844, vol. i. p. 643, it is re-

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marked, that it is possible that the crystalline form and isomorphism are not in any degree the indication of atomic constitution, or even intimately and necessarily connected with it, but arise from an accidental character of bodies, by which a simple atom may happen to resemble a compound one. This view is suggested by the fact, that a simple atom of potassium is isomorphous through a long series of compounds with the group of five atoms which constitute ammonium. This circumstance, as well as the isomorphism of the cyanogen and chlorine compounds, at least clearly shows that the compound radicals have an equal value in reference to isomorphism with the simple radicals or elements.

All previous arguments in favour of the hypothesis of polymeric isomorphism have been founded upon facts derived from inorganic chemistry, and yet it is probable that these relations occupy a more important place in the organic world than in the inorganic. There is no doubt that it is among organic compounds in which vicarious constituents do not occur, as in inorganic bodies, and where consequently the mode of formation may be more easily traced, and the resulting products are more definite, that the most striking instances of polymeric isomorphism might be obtained, if it were possible on the one hand to prepare readily measurable crystals, and if on the other a crystallographic determination of all measurable organic crystalline compounds had been made.

I. In the study of the decomposition-products of organic bodies, an analogy in composition has frequently presented itself between a great number of bodies which could not be detected by direct analysis. This relation between bodies has been called homology. Gerhardt calls all those bodies homologous which differ from each other by $n(C^2H^2)$, and lays down the empirical law, that when two bodies have such compositions that the one may be expressed by that of the other, $+n(C^2H^2)$, they have both analogous characters, *i.e.* similar relations of combination and decomposition. If this analogy of characters extends itself to the form of the crystals, the law may be thus expressed:—All organic bodies which belong to an homologous series are isomorphous.

If this law is shown to obtain, if C^2H^2 can be replaced by $n(C^2H^2)$, or what is the same thing H by $CnH(n+1)$, without alteration of the form of the crystal, it would be a proof in favour of Scheerer's hypothesis.

Lies found the formula of the butyrate of copper $C^8(H^7Cu)O^4 + HO$. The acetate of copper crystallizes with the same proportion of water. Lies then observed that both salts were isomorphous. If we adopt Kolbe's view of the two acids belonging to one and the same homologous series, according to which acetic acid $= C^2H^3C^2.O^3.HO$, and butyric acid $= C^6H^7{\frown}C^2.O^3.HO$, then C^2H^3 will have been replaced by C^6H^7. This would therefore be the first example of the polymeric isomorphism of homologous compounds.

There are parallel series of homologous bodies, with regard to which it is frequently doubtful whether a body belongs to one or the other. In such a case, the crystallographic characters alone

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would often suffice to determine the question if the above empirical law obtains. Thus, for example, the parallel series—

Piperine.....	$C^{34}H^{19}NO^6$	Morphine	$C^{34}H^{19}NO^6$
Pelosine.....	$C^{36}H^{21}NO^6$	Codeine	$C^{36}H^{21}NO^6$

Piperine belongs to the oblique prismatic system, codeine to the rhombic. If now piperine is isomorphous with pelosine, proof is afforded on the one hand that both in fact belong to one homologous series; on the other hand, the polymeric isomorphism would serve to corroborate the formula of piperine. If we assume that piperine is isomorphous with pelosine, we know that the formula of pelosine, according to the investigations of Bœdeker, is $C^{36}H^{21}NO^6$, and that of piperine would consequently be $C^{34}H^{19}NO^6$ (Laurent), and not $C^{70}H^{37}N^2O^{10}$ (Wertheim).

It is generally admitted that—

Glycocolle	$C^4\ H^5\ NO^4$
Alanine.....	$C^6\ H^7\ NO^4$
Leucine	$C^{12}H^{13}NO^4$

belong to a homologous series. Of these three bodies the crystals of glycocolle only have been measured. The measurement of the crystals of alanine was, according to Strecker, not possible, on account of the roughness of their planes. But a knowledge of their angles would have been of great interest, as they afford a means of determining to what homologous series the body belongs. A knowledge of the angle would, in the case of this series, have shown at once whether alanine ought to be placed between glycocolle and leucine, and whether sarcosine, which previously occupied this place, must be removed.

It is perhaps possible in this way to find evidence in favour of this law by the determination of the crystalline forms of the members of a parallel homologous series:—

Urethylane (methylurethane)....	$C^4\ H^5\ NO^4$
Urethane (æthylurethane)	$C^6\ H^7\ NO^4$
Amylurethane	$C^{12}H^{13}NO^4$

These compounds may be considered as consisting of the bases homologous with ammonia and 2 equivs. of carbonic acid.

The discovery of these bases has already led to valuable results, and will do so even more when the forms of the compounds derived from them have been studied. When the crystalline form of any ammonia compound is known, the crystalline form of the compound of the corresponding ammonia base should be the same if the above law obtains.

The crystalline form of the ammonio-chloride of platinum, NH^3, ClH, $PtCl^2$, is known. That of the amyl-ammonio-chloride of platinum, $C^{10}H^{13}N$, ClH, $PtCl^2$, *i. e.* a compound in which 1 atom H is replaced by 1 atom $C^{10}H^{11}$, is the same, a regular octohedron. If the double platinum salt is now prepared with an amide or imide base, for example triæthylamine, giving the compound—

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$$\left.\begin{matrix} C^4\,H^5 \\ C^4\,H^5 \\ C^4\,H^5 \end{matrix}\right\} N,\ ClH,\ PtCl^2,$$

it ought also to crystallize in regular octohedrons.

The aniline compounds, which are remarkable for their great tendency to crystallize, would probably be better adapted to determine the accuracy of the above law. According to it, the aniline-chloride of platinum, $C^{12}\,H^7\,N,\ ClH,\ PtCl^2$, is isomorphous with methyle-aniline-chloride of platinum, $C^{14}H^9\,N,\ ClH,\ PtCl^2$, æthyle-aniline-chloride of platinum, $C^{16}\,H^{11}\,N,\ ClH,\ PtCl^2$, bi-æthyle-aniline-chloride of platinum, $C^{20}\,H^{15}\,N\ ClH,\ PtCl^2$, and so on, but probably not isomorphous with the parallel isomeric toluidine and xyloidine compounds. If aniline is considered as phenylamine—

$$\left.\begin{matrix} C^{12}\,H^5 \\ H \\ H \end{matrix}\right\} N,$$

there will have been a replacement in the double platinum salt of H by $C^2\,H^3$, $C^4\,H^5$, or of 2H by $2C^4\,H^5$, without any alteration of the crystalline form. Hofmann has recently obtained the body hydrated oxide of tetra-æthyle-ammonium—

$$\left.\begin{matrix} C^4\,H^5 \\ C^4\,H^5 \\ C^4\,H^5 \\ C^4\,H^5 \end{matrix}\right\} NO,\ HO,$$

crystallizing with 4 atoms of water, and resembling in its behaviour the compound $KO,\ HO + 4HO$. If it were possible to determine the crystalline form of the two compounds, it is probable that they would be found isomorphous, which would be a striking example of the truth of polymeric isomorphism. In this case there would have been a replacement of 1 atom of potassium by 1 atom of the compound $C^{16}\,H^{20}\,N$, which Hofmann compares with ammonium, and very appropriately calls an organic metal.

On account of the hygroscopic character of this hydrated oxide of tetra-æthyle-ammonium, the determination of its crystalline form is impossible, and it cannot therefore be employed as an evidence in favour of polymeric isomorphism; but this would perhaps be possible if it were combined with cyanic acid, and then converted into urea, and quadri-æthyle-urea,

$$C^2 \left.\begin{matrix} C^4\,H^5 \\ C^4\,H^5 \\ C^4\,H^5 \\ C^4\,H^5 \end{matrix}\right\} N^2\,O^2,$$

which should be isomorphous with ordinary urea, $C^2\,H^4\,N^2\,O^2$.

The compound aniline-ureas obtained by Wurtz would be still better adapted to this purpose; they would, among other things, show whether the organic base flavine, $C^{26}\,H^{12}\,N^2\,O^2$, obtained by Chancel from the products of the dry distillation of benzoate of

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lime, is really bi-aniline-urea, that is ordinary urea in which 2 atoms H have been replaced by 2 atoms $C^{12}H^{5}$=phenyle.

Thialdine, $C^{12}H^{13}NS^{4}$, is a body which of all those compounds resulting from ammonia is the most readily crystallizable; the discoverers of thialdine state that it crystallizes in the form of gypsum. It would be easy, by the action of sulphuretted hydrogen upon the compounds of aldehyde with methylamine, æthylamine, amylamine, &c., to obtain the bodies homologous with thialdine—

$$C^{14}H^{15}NS^{4}$$
$$C^{16}H^{17}NS^{4}$$
$$C^{22}H^{29}NS^{4},$$

and to determine their crystalline form.

The murexides of the ammonia bases might also be capable of measurement. It is extremely probable that, in the preparation of these bodies, the murexoine of Rochleder would be met with.

II. There are still other compounds, the accurate study of which may be made available for the above purpose. The existence of the alcoholates of Graham cannot be doubted, notwithstanding the question which Einbrodt has raised as to whether these bodies may not really be mixtures of crystals of a hydrated salt with an alcoholic solution of the salt. The investigations of Graham are at all events trustworthy; and Chodnew has moreover recently instituted researches upon the alcoholates, from which it is clearly proved that there are compounds of salts with alcohol in which the water of crystallization is replaced by alcohol. Einbrodt, in a recent paper, expressed himself decidedly against the alcoholates, and adduces, among other arguments, the fact that salts with water of crystallization have a definite form, but that this had not been found to be the case with any alcoholate. But whatever is true of alcohol applies equally to wood-spirit, and *vice versâ*. Schweitzer availed himself of the fact of wood-spirit forming a definite compound with chloride of calcium, which is not decomposed at 212°, for the purpose of separating it from xylite and mesite, by digesting the mixture of these liquids with fused chloride of calcium, distilling off the xylite and mesite in a water-bath, and decomposing the remaining compound, a methyle-alcoholate, with water. The author had occasion, a few years since, to prepare hydrated oxide of methyle from raw wood-spirit according to Schweitzer's method, and found that the methyle-alcoholate crystallized out of the liquid in long crystals, apparently six-sided prisms. It was not possible to analyse the compound. The mixture of the three liquids had previously been distilled repeatedly over caustic lime, so that it could not contain any water. A replacement of the water by wood-spirit had therefore taken place without any visible alteration of the crystalline form. We do not indeed know whether the replacement was atom for atom, but it is certain that HO was replaced by $C^{2}H^{4}O^{2}$. We may consider the latter body, irrespective of its actual constitution, as consisting of $C^{2}H^{2}+2HO$. But if HO is replaced by such a complex atom, it is a proof of isomeric isomorphism. It seems as if a few alcoholates

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contained only half as many equivalents of alcohol as the corresponding hydrated salts contain equivalents of water. This may perhaps afford confirmation of Williamson's view, according to which the formula of alcohol ought to be halved.

III. The most important results for crystallo-chemistry may be looked for from the comparison of the crystals of the substitution products with those of the original bodies. It is very probable that by this means numerous cases of isomorphism (in the replacement of H by Cl) and polymeric isomorphism (in the replacement of H by NO^4) would be met with if the limits between which homœomorphism is still to be assumed are somewhat extended. There are established instances in which a substance is homœomorphous with its chlorinated product. The determination of the crystalline forms of Erdmann's isatine and chlorisatine by G. Rose lead to an approximation in the value of the angles of the crystals of both bodies.

De la Provostaye compared the crystalline form of oxamethane (oxamate of oxide of æthale) with that of chloroxamethane, and found that both compounds were isomorphous, or rather that their forms were secondary modifications of the same fundamental form. According to Mitscherlich, however, the otherwise complete identity of form which constitutes isomorphism was not observed; and it was only the angles of the terminal planes, but not those of the lateral planes, which corresponded with each other. According to Laurent, phenylic acid (phenole, hydrated oxide of phenyle), $C^{12}H^6O^2$, is isomorphous with its substitution-products, especially with the mono- and bichlorophenylic acids (chlorospirolic acid), with the di- and trinitrophenylic acid (nitrophenisic and nitrophenic acid); the dinitrophenylate of ammonia is also isomorphous with the trinitrophenates (picrates) of ammonia and potash. According to Laurent, the following bodies are isomorphous throughout the whole of these compounds:—

Cl with H, NO^4 (=X) and Br.	K with H.
NO^4 with H and Br.	KO with HO.
Br with H.	NH^4O with HO and KO.

It may be expected that the recently-discovered monitrophenylic acid of Hofmann will prove to be, in the same way as the other substitution-products, isomorphous with phenylic acid. From an observation which may be mentioned here, it has moreover been ascertained that chloride of æthyle crystallizes at a temperature of −0·4°—4°F., in remarkably distinct cubes; from whence it follows that æthyle, C^4H^5, is isomorphous with K. This admitted, however, it is evidently necessary to assume with Gerhardt, the existence of different allotropic conditions of hydrogen; the hydrogen of water must be in another form than that of ammonia; while we see here that C^4H^5 is isomorphous with K and with H^4 of ammonium, it appears to follow, from an instance mentioned above, that $4(C^4H^5)$ may also be isomorphous with K and with H.

The observation of Heintz with regard to the crystals of creatine

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and creatinine is of great importance to crystallo-chemistry. The crystals of creatine ($C^8 H^9 N^3 O^4 + 2HO$) have the same relation to those of creatinine ($C^8 H^7 N^3 O^2$) as those of augite to those of hornblende. Both crystals have nearly the same angle of inclination between the principal axes and the clino-diagonals. The latter are in the proportion of 2 : 1 with the same ortho-diagonal. It follows therefore that there are bodies, which, when another complex atom is combined with them, change their crystalline form only in such a way that the one axis is altered in its length.—*Journ. für Prakt. Chem.*, vol. liii. 449–459.

On Hæmatoidine and Bilifulvine. *By* M. VIRCHOW.

The author refers to Reichert's paper, showing that our knowledge of the formation of crystalline compounds has been importantly extended by the discovery of the existence of an albuminous substance in a crystalline form. In a substance resembling in appearance dried blood, probably deriving its origin from an extravasation of this liquid, which covered the surface of the placenta and the membranes of an almost mature fœtus of a guinea-pig, as also the adjacent mucous membrane of the uterus, Reichert found tetrahedral crystals. They were of a blood-red colour, and appeared to consist of a proteine substance impregnated with hæmatine. Although their other chemical and physical properties, which are very remarkable, did not exhibit any important relation to the crystals of hæmatoidine, yet there is no doubt that their genetic similarity is very great. If Reichert's view, that crystallization is a property inherent to the proteine substance, should be confirmed, it would also become a question in regard to the crystals of hæmatoidine, whether their formation ought not to be ascribed to the concurrence of the proteine substance. The colouring matter would then hold the same relation in them as *e. g.* the colouring metallic salts in crystals of quartz, the proteine substance alone forming the crystalline skeleton, and the colouring matter a merely mechanically-mixed ingredient. Wherever hæmatoidine is being formed, hæmatine and some proteine substance are present. Hence the author's conclusion, that hæmatoidine is a compound of both. The author showed, on a former occasion, that after treating the pigment-crystals with various chemical reagents, amorphous granular flakes result, and which, in many cases, on the formation of the pigment in amorphous proteine matter, surrounds the coloured grains as a colourless envelope. He also showed that crystals of hæmatoidine may be formed under three circumstances,—1st, in cells; 2nd, in amorphous proteine matter (in both cases arising from diffused hæmatine); 3rd, from aggregations of blood-corpuscles, which fuse together without diffusion of the hæmatine, and undergo change simultaneously.

With regard to Henle's supposition, that hæmatoidine is of a fatty nature, the author remarks that fat has no doubt a peculiar attraction for this substance, and seems in some manner to favour its formation by promoting the metamorphosis of hæmatine; but he believes that

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it is not of a fatty nature, and that the occurrence of coloured drops of fat, after treating masses of hæmatoidine with mineral acids, proves nothing, because in this case the fat is colourless, and its surface is either covered with a coloured layer, or the coloration is only apparent, probably arising from mere reflexion. It differs crystallographically from cholesterine, besides which it is often found simultaneously with this substance, as in cysts of the thyroid gland. Its crystalline form is also entirely different from that of stearine; and besides, pure crystals of the latter have not yet been found in the human body.

His investigations of the derivatives of hæmatine, especially hæmatoidine, led him to comparisons with the colouring matter of the bile, and to the question of its origin from the colouring matter of the blood. The great similarity between hæmatoidine and cholepyrrhine, rendered it desirable first to procure crystals of cholepyrrhine. Berzelius once only obtained small reddish-yellow crystals from the bile, which he denominated bilifulvine; and Bizio found emerald-green rhomboidal crystals in morbid bile, to which he gave the name of erythrogen. The author once found, in and upon the wall of the sacs of Echinococci in the liver, hæmatoidine and semi-crystalline grains and lumps of cholepyrrhine. Since this he has repeatedly found crystals corresponding to bilifulvine in the liver and in the bile, and principally under two circumstances, retention of the bile and chronic catarrh of the gall-bladder. The colouring matter of the bile becomes precipitated upon the altered mucus, subsequently undergoes further alterations, and with the altered mucus forms the basis of gall-stones. Simultaneously, probably in consequence of the decomposition of the fatty acids and cholates by a newly-formed acid, free drops and crystals of fat are formed, the latter of which sometimes, but rarely, exhibit the small acicular bundles of margaric acid, but most frequently the well-known plates of cholesterine. The bile then appears as a thickish, sometimes almost pasty and lumpy mass, of a dark brown colour, in which peculiar small dark points are distinguishable. Under the microscope, the crystals of bilifulvine are frequently found, especially at these spots; they form longish, very fine needles, always of a yellowish-red colour. They are usually single, or several combined. At first sight it appears that most of them have a thick globular extremity, and a very fine capillary point; and they very often have a curved, variously-bent and twisted form, thus resembling the lithate of ammonia. Closer examination shows that these appearances result from the needles consisting of an aggregation of smaller crystals, variously superimposed and combined with drops of fat and plates of cholesterine.

The needles of bilifulvine react in a totally different manner from those of hæmatoidine; yet there is some resemblance. Caustic alkalies, especially potash, dissolve them tolerably readily. When the solution is neutralized and acidified, no separation of crystals occurs, nor is there any precipitate. Acetic acid produces no change. Concentrated sulphuric acid, when acting slowly, gradually attacks the needles, which at first become dark; in a current of it, a reddish-

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yellow circle first forms around them, and the whole then vanishes. Nitric acid has but little action upon them, except when the action is very intense, when they are decomposed. From these experiments, bilifulvine belongs to the granular pigments, and probably holds an intermediate place between hæmatoidine and melanine. Chemical investigation shows that these crystals are not formed by the deposition of colouring matter upon crystals of margarine and filaments of fungi. Æther removes the drops and crystals of fat, and leaves the needles unchanged; whilst potash and sulphuric acid destroy the needles, and leave the fungi unaltered.—*Ann. der Chem. und Pharm.*, June 1851.

On some Combinations of the Alkaloids with Tartaric Acid. By M. Arppe.

Tartrate of Morphine, $C^{35}H^{20}NO^6, HO, C^4H^3O^5$.—When morphine is added to a solution of bitartrate of potash until the solution is neutral, some bitartrate of potash first separates, and then tartrate of morphine, while neutral tartrate of potash remains in the solution. When morphine is digested with a solution of tartaric acid until the liquid has a neutral reaction, verrucoid groups of crystals, similar to the preceding, and consisting of concentrically-arranged groups of needles, separate on slow evaporation. They effloresce externally at about 68° F., but do not part with the entire amount of their water of crystallization below 266°.

The salt is readily soluble in water, and likewise in alcohol. Neither caustic nor carbonated alkalies cause a precipitate in the aqueous solution; and the same is the case with chloride of calcium, unless the solution is mixed with caustic potash; ammonia does not behave in this respect like potash. The most remarkable property of this salt is, that, on being heated to 266°–284°, it exhibits electrical polarity, which it retains for more than an hour after it has become perfectly cold. A small granule of the effloresced salt is gradually projected several inches. The same phænomenon is exhibited every time it is heated. The salt prepared with bitartrate of potash contained 6·824 per cent. of water, the other 6·496, 6·553, 6·41; the above formula requires 6·853 per cent. Laurent's formula, $C^{34}H^{19}NO^6$, gives a much greater difference in the amount of water.

Bitartrate of Morphine, $C^{35}H^{20}NO^6, HO + 2C^4H^3O^5, HO$ (dried), crystallizes readily from acid solutions, being far more soluble than the neutral salt. It is obtained by mixing the base and acid in equivalent proportions, &c. in smooth rectangular prisms. The salt loses about 2 per cent. of water before it begins to be decomposed, which takes place below 284°. On cautiously applying heat, a small portion may be melted without decomposition. When dried in the air, the salt contains one more equivalent of water than is given in the above formula; it loses up to 212°, 1·99 per cent.; from thence to 248°–284°, so much more that the entire loss amounts to 2·43 per cent.

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Tartrate of Strychnine, $C^{44}H^{24}N^2O^4, HO, C^4H^2O^5 + 4HO$.—Strychnine behaves like quinine towards tartrate of potash; when the solution of the latter has been saturated with the alkaloid, shining needles more than an inch in length separate, which dissolve in water and in weak alcohol. The same salt is obtained from a neutral solution of strychnine in tartaric acid; it effloresces in the air without falling to a powder, becomes anhydrous at 266°, and may be heated to 302° without further loss.

The salt prepared from bitartrate of potash gave in one experiment 7·76 per cent. of water, and left on ignition an exceedingly small residue of carbonate of potash. The strychnine is precipitated from a solution of the salt by potash and ammonia. Chloride of potassium gives no precipitate. The salt prepared with tartaric acid contains 7·588 per cent. of water of crystallization; the above formula requires 7·588.

Bitartrate of Strychnine, $C^{44}H^{24}N^2O^4, HO, C^4H^2O^5 + HO, C^4H^2O^5 + 6HO$, is the salt which separates when an excess of tartaric acid is employed. The slender acicular crystals, which have a strong lustre even when dry, do not effloresce in the air, and are not very soluble in water; potash produces no precipitate at first, but after a time causes a considerable opacity. A portion of the water of crystallization is expelled at 212°, but it does not part with the whole below 257°; it may then be heated without further loss to 302°. The air-dried salt gave at 257°, 284°, 302°, the same amount of water, viz. 10·11 per cent.

Tartrate of Quinine, $C^{20}H^{12}NO^2, HO, C^4H^2O^5$.—Quinine dissolves with difficulty in a solution of bitrartrate of potash; on evaporating the solution, a mixture of bitartrate of potash and a crystalline salt of quinine separates. When an acid solution of quinine is neutralized with potash, slender acicular crystals of tartrate of quinine are obtained on evaporation, contaminated with the acid potash salt; the mother-liquor finally deposits neutral tartrate of potash. The salt, which quinine forms in preference with tartaric acid, is easily obtained by decomposing sulphate of quinine with neutral tartrate of potash, when a distinctly-crystalline powder separates; this has a bitter taste, a neutral reaction, is sparingly soluble in water, and melts, when carefully heated, without decomposition. At 266°–293°, it lost 1·5 per cent. of water, and did not effloresce. It appears to be anhydrous.

When tartaric acid is neutralized with quinine, only a gum-like mass is obtained on evaporation. If the acid is in excess, an acid salt crystallizes from the thick mother-liquor, which, owing to its ready solubility, could not be separated for closer examination. The solution has an acid and bitter taste, and exhibits a blue and red opalescence. When heated, the salt melts, turns yellow, and becomes resinous. The above formula requires 81·2 per cent. of quinine. Laurent's formula, $C^{38}H^{22}N^2O^4$, being admitted as correct, and the salt supposed to be neutral $= C^{38}H^{22}N^2O^4, HO, C^4H^2O^5$, requires 80·52 per cent. Potash separated from a solution of the salt 79 per cent. of quinine; and as it was found that the potash

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dissolves some quinine, the author concludes that the first formula is most correct.

Tartrate of Cinchonine, $C^{20}H^{12}NO^2$, HO, $C^4H^2O^5 + C^{20}H^{12}NO^2 + 2HO$.—Free tartaric acid behaves in the same manner to cinchonine as to quinine. On neutralizing bitartrate of potash with cinchonine, which dissolves readily and in abundance, there is formed, on cooling or evaporation, a considerable number of tolerably large acicular crystals, grouped in fascicles. They are very sparingly soluble in water, not altered in the air, and do not part with their water of crystallization below 212°–248°. In the anhydrous state, they exhibit electrical polarity, like the salt of morphine, only weaker. The whole of the cinchonine can be precipitated from its solution by potash. The air-dried salt lost up to 248°–257°, 4·69 and 4·62 per cent. of water, and nothing more then up to 356°, at which temperature it begins to decompose. The above formula requires 4·49 per cent. of water. Laurent's formula, $C^{38}H^{22}N^2O^2$, requires 4·65, admitting the salt to be $C^{38}H^{22}N^2O^2$, HO, $C^4H^2O^5 + 2HO$.

Tartrate of potash forms no double salts with the alkaloids.—*Journ. für Prakt. Chem.*, li. p. 331.

On the Occurrence of Amygdaline. *By* W. Wicke.

Amygdaline appears to be much more generally distributed, and to have a far greater importance in the physiology of plants than was formerly supposed. From the investigations of the author, which were made in May, it follows that it is an almost universal constituent of the Pomaceæ. Its detection was effected by distilling parts of the different plants with water, and testing the distillate for hydrocyanic acid. By this means it was detected in the young shoots with the still unopened leaves, in the petioles, and especially in the bark of *Sorbus aucuparia*, in the bark and young shoots of *Sorbus hybrida*, in the shoots and blossoms of *Sorbus torminalis* (in much less quantity here in the leaves, petioles and bark), in the leaves, young fruit, young shoots, and very abundantly in the bark of *Amelanchier vulgaris*, in the very young shoots of *Cotoneaster vulgaris* (none in the bark, flowers or leaves), in the very young shoots of *Cratægus oxyacantha* (at a later period in no part), in the very young shoots of *Prunus domestica* (at a later period in no part), in every part of *Prunus padus*, and in such large quantity in the leaves that globules of bitter almond-oil separated from the distillate. On the other hand, it could not be detected in the green orange; the roots, branch, bark, leaves, young shoots or fruit of *Prunus cerasus*, in whose kernels it is known to be present; nor in the leaves or bark, &c. of *Prunus mahaleb* and *Pyrus malus*.—*Ann. der Chem. und Pharm.*, vol. lxxix. p. 79.

On the Double Cyanide of Potassium and Silver, and on the part it plays in Electro-plating. *By* H. Bouillet.

When any salt of silver is placed in contact with cyanide of potassium, a curdy precipitate of cyanide of silver and a salt of

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potassium are formed; on adding an excess of the reagent, the precipitate dissolves, and a crystalline salt, called the double cyanide of potassium and silver, is obtained. In a dilute liquid, the salt crystallizes in small detached rhombohedra. According to the experiments of Messrs. Glassford and Napier, the formula is CyK, CyAg+HO. From a concentrated solution it separates in the form of little hexagonal crystals; it contains no water in this case; its formula is CyK, CyAg.

But whatever their crystalline form, the solution of these salts acts in the same manner upon substances with which they are brought into contact. Among the most remarkable properties of this solution, I may mention one which has long been known. When submitted to the influence of the battery, metallic silver is deposited on the metal placed at the negative pole in the form of a continuous adherent coating; and there is dissolved at the positive pole, where a strip of metal has been placed, an amount of metal nearly equivalent to the quantity of silver deposited.

It is well known, that, on placing a salt of silver in contact with yellow or with red prussiate of potash, solutions are obtained which are decomposed in the same manner by the influence of the battery. But it was important to ascertain whether in these prussiates it was not the solution of the same double salt in water which caused the silvering, and whether in the liquids formed with the ferruginous prussiates the iron was an element essential for the success of the operation, as some chemists, especially Messrs. Ruolz and Flandin, have thought. Was it not more likely that the iron was wholly masked and without influence on the results, in accordance with the facts so well demonstrated by Gay-Lussac?

I made a bath so that the proportions employed, although different, should not deprive the liquid of the property of silvering, for instance, 1 part of yellow prussiate to 8 parts of cyanide of silver. Solution resulted after some time, and in the liquid a blue precipitate was formed; on filtration, it was colourless, and contained a crystallizable salt. The solution silvered, but nevertheless qualitative analysis only showed the presence of cyanogen, potassium and silver; the iron consequently was completely eliminated. Determining the silver as chloride, the potash as sulphate, the carbon and nitrogen by burning the substance with chromate of lead, I obtained the following results:—

Silver	54·33	1 =	54·27
Potassium.....	19·63	1	19·60
Cyanogen	26·65	2	26·13

Consequently the formula to be assigned to these salts was CyK, CyAg. This formula is the more certain if we calculate the weight of the double cyanide from the weight of the sulphate found;

we have $0{\cdot}634 : x :: 243 : 199 \qquad x = 0{\cdot}519,$

instead of 0·520, the number employed; clearly showing that the formula of the salt is CyK, CyAg. It is now certain that the agent of the silvering in the yellow prussiate is the double cyanide of potas-

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sium and silver. By what reaction has it been formed? This is the question I have endeavoured to solve experimentally.

When a salt of silver is placed in contact with ferrocyanide of potassium, a salt of potassium and ferrocyanide of silver are formed. This latter is very unstable, and it readily decomposes, in contact with the air, into protocyanide of iron and cyanide of silver. The cyanide of silver acts like a salt of silver, and reforms ferrocyanide of silver and a salt of potassium, which is the simple cyanide of potassium. This latter forms, in contact with the cyanide of silver, the double salt, which alone is soluble, whilst the other elements remain in the state of precipitate, or fall on cooling. By carrying out the reaction protected from the air, the precipitate remained ray; in contact with the air, it became blue; treated with an acid or with chlorine, it became still more blue, while potash turned it brown; it was therefore protocyanide of iron. The following equation expresses the reaction:—

$$2CyAg + Cy^3\,FeK^2 = 2CyK, CyAg + CyFe.$$

I repeated these experiments on the red prussiate. The baths were prepared in the same manner, and the results were the same; the iron was eliminated, and the liquid silvered. The crystallized salt furnished on analysis—

Silver	53·98	1 =	54·27
Potassium	19·68	1	19·60
Cyanogen	26·68	2	26·13

Calculating the weight of the double cyanide from the weight of the sulphate found, we have $533 : x :: 243 : 199$, $x = 0{\cdot}438$, instead of 0·440, employed, a result which shows clearly that the formula of the salt is CyK, CyAg. In the red prussiate, as in the yellow prussiate, and in the white one, the salt which effects the electro-plating is the double cyanide of potassium and silver.

On producing the reaction protected from the air, the precipitate became brick-red, with disengagement of hydrocyanic acid. The precipitate was nothing further than peroxide of iron.

From the ultimate products of the reaction, it may be concluded that it is of the same nature as with the yellow prussiate, only instead of protocyanide of iron being formed, as in the first case, sesquicyanide is produced. The reaction may be expressed by the formula—

$$3CyAg + Cy^3\,K^3, Cy^3\,Fe^2 = Cy^3\,Fe^2 + 2CyK, CyAg.$$

We therefore again see that the silver does not precipitate, properly speaking, the iron from these cyanogen compounds; but in consequence of the general reaction of metallic salts upon the ferrocyanides, and of the cyanide of potassium on the ferrocyanide of silver, discovered by Messrs. Glassford and Napier, the cyanide of silver combines with the cyanide of potassium which it had set free.

In conclusion, whether cyanide, ferrocyanide, or ferridcyanide of potassium is employed to form a bath for electro-plating, by adding to one of these salts some cyanide of silver, or any other salt of

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silver, there is always obtained a solution of the double cyanide of potassium and silver. In all three cases it is this solution which effects the silvering; in all three cases the agent is the same, and possesses the same properties, although the substances employed to produce it differ.—*Comptes Rendus*, Dec. 1, 1851.

On a peculiar Acid secreted by the Pulmonary Parenchyma. *By* F. Verdeil.

I have succeeded in extracting from the pulmonary parenchyma of most animals a peculiar acid, which crystallizes, and forms with bases crystalline compounds. This acid is secreted by the parenchyma of the lungs; it occurs in part in the free state, but the greater proportion combined with soda. The following process was adopted to isolate it:—The tissue of the lung is chopped very fine, then rubbed in a mortar with cold distilled water; the liquid pressed through linen has a distinctly acid reaction. The liquid is heated in the sand-bath to coagulate the albumen it contains, then neutralized with baryta-water, and evaporated on the water-bath; when reduced to three-fourths of its primitive bulk, a solution of sulphate of copper is added to it, which determines a bulky precipitate. The filtered liquid contains an excess of sulphate of copper. It is removed by adding a little of a solution of sulphuret of barium; an insoluble precipitate of sulphate of baryta and sulphuret of copper is formed. The filtered liquid is evaporated until crystals of sulphate of soda separate, when a little dilute sulphuric acid is added; the whole then treated with boiling absolute alcohol, which dissolves out the acid of the lungs, leaving an insoluble residue of sulphate of soda. In the course of a few hours after the cooling of the alcohol, groups of concentrically-arranged acicular crystals separate.

By the addition of the sulphate of copper, a number of substances, such as fats, non-coagulated albumen, &c., which would prevent the acid being isolated, are removed. The acid thus obtained in a crystalline state is a very brilliant substance, which strongly refracts the light. Heated to 212°, it does not part with any water of crystallization; at a higher temperature it decrepitates and fuses, then decomposes, giving rise to empyreumatic products and a bulky cinder, which disappears without leaving a trace of ash. It is very soluble in water, insoluble in cold, but soluble in boiling alcohol, and insoluble in æther. It contains, according to elementary analysis, carbon, hydrogen, nitrogen, sulphur, and oxygen in definite proportions.

The acid of the lungs forms crystallizable salts with the bases, and expels carbonic acid from the carbonates.

The presence of an acid secreted by the parenchyma itself of the lungs appears to us of considerable physiological importance. The acid is secreted in contact with the carbonate of soda of the blood conveyed by the capillary vessels; it decomposes that salt, and combines with the soda, while the liberated carbonic acid is given off by respiration. The presence of a portion of the acid in the

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free state in the lungs shows that it is formed there, and not in the blood, which is alkaline. On uniting with the soda of the blood, the acid does not alter its reaction, as it merely takes the place of the expelled carbonic acid.

The author promises the analysis of the acid and salts on an early occasion.—*Comptes Rendus*, Dec. 1, 1851.

On the Deportment of Organic Colouring Matters towards Sulphurous Acid. *By* Prof. C. F. Schönbein.

Some time ago*, the author showed that oxygen, under the joint influence of sunlight and various organic substances, such as æther, oil of turpentine, sulphurous acid, &c., acquires the property of decomposing a solution of indigo in sulphuric acid. Under these circumstances sulphurous acid is able to destroy 125 grms. of an indigo solution, which would require 2 grms. of the strongest nitric acid to effect the same purpose.

The alteration which the indigo dissolved in the sulphuric acid experiences in this operation is precisely the same as is produced in this pigment by ozone, oxygen exalted by light, peroxide of hydrogen, oxygenated oil of turpentine, &c. Hence, when a piece of linen dyed with indigo-solution is bleached with a mixture of gaseous sulphurous acid and atmospheric air, rapidly in sunlight, but slowly in the dark, the phænomenon must be explained in a very different manner from the decolorization of a red rose, &c.

Schönbein shows in this paper that—

1. The pigments of the majority of blue and red flowers, fruits, &c. form colourless compounds with sulphurous acid.

2. The pigments of yellow flowers are indifferent towards sulphurous acid, and are not bleached by it.

3. Indigo-blue, cactus-red, and the yellow colouring matter of silk, are bleached by sulphurous acid, owing to the oxygen of the latter (especially under the joint influence of light) being applied to the oxidation, *i. e.* destruction of the three pigments above mentioned.

4. The bleaching of substances impregnated with organic colouring matters by means of sulphurous acid results from two very different causes. In a few cases the pigment is actually destroyed by oxidation, but in most cases it is merely masked.

When a skein of deep yellow raw silk is suspended in a white bottle containing the above-mentioned gaseous mixture, and kept in a perfectly dark place, the silk is very slowly bleached, and months elapse before it has become perfectly white. Those threads which are directly exposed to the solar light are perceptibly bleached in the course of a few hours, and completely so after some days, while the inner threads still retain their original yellow colour. In this case the colouring principle is found to be destroyed. Fresh flowers of different species of Cactus, as *C. speciosissimus*, *C. phylanthus*, &c., are completely bleached in four or five hours in the above

* Philosophical Magazine for July 1851.

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gaseous mixture when exposed to the powerful light of a June sun; and likewise in the dark, only somewhat slower. The colour of the flowers which has disappeared cannot be reproduced by any means.

If the red pigment be extracted by means of water containing acetic or hydrochloric acid from the flowers of *Cactus speciosissimus*, and the bluish-red liquid mixed with an aqueous solution of sulphurous acid, no alteration of colour results; but if the mixture be shaken with atmospheric air and exposed to the light, the colour gradually becomes paler, and finally disappears entirely. The same decoloration, or rather destruction, likewise takes place in the shade, but less rapidly.

Schönbein has submitted a large number of blue and red flowers and fruits, for instance, blue-bells, salvias, roses, pinks, poppy, dahlias, violets, strawberries, raspberries, &c., to the action of gaseous sulphurous acid; they were all decolorized more or less quickly. No oxygen is here necessary, and it takes place in the dark as rapidly as in sunlight; the bleaching of these flowers and fruits is totally different from that of the Cactus flowers, of the linen dyed with indigo, and of the yellow silk. We are able to restore the colour of these flowers by means of several reagents, which is not the case with respect to the latter; for instance,—

1. *Ozone* restores the red of pinks, roses, poppy, raspberries, &c. which have been bleached with sulphurous acid, in less than an hour.

2. *Oxygen with the joint influence of light* resembles ozone in this respect. A bleached rose, &c., placed with its stalk in water, and exposed to the action of pure oxygen or atmospheric air turns red very slowly in the dark, while in sunlight it proceeds far more rapidly, although not so quickly as in ozonized air. The colour of a rose, bluebell, or larkspur is completely restored in atmospheric air in the course of a sunny day.

3. *Oxygen charged with the vapour of æther, or oil of turpentine, and light.*—When a bleached rose, strawberry, &c. is suspended in a white bottle filled with oxygen or atmospheric air, and the bottom of which is just covered with some pure æther, pure oil of turpentine, or oil of lemons, and the vessel placed in the dark, the flowers appear unaltered after twenty-four hours; but if the bottle be exposed to the light of the sun, those parts of the flowers which are immediately exposed to the light first become coloured, and after a few hours the roses, &c. are just as red as if they had been submitted to the action of ozonized air.

4. *The oxidating principle produced in the slow combustion of æther.*—If a bleached strawberry or rose, &c. be suspended in a wide-mouthed bottle, capable of holding a quart, filled with air, and containing a little water, and a few grammes of æther, they continue white for a long time in the dark; but if a spiral of platinum wire, heated not quite to redness, be dipped several times into the air charged with æther, the flowers and fruit reacquire their original colour.

5. *Oxygenized essential oils, or oxygenized æther.*—These act in the same manner as ozone, and restore the colours of the flowers

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and fruit bleached by sulphurous acid in the dark as rapidly as in the light.

6. *Oxidated water* behaves in the same manner as oxygenated oil of turpentine and the other essential oils.

7. *Sulphurous acid and oxygen.*—When a bleached rose is suspended in a bottle containing a moist mixture of gaseous sulphurous acid and oxygen or atmospheric air, the flower gradually becomes red again, in less time in sunlight than in the dark. The fact that most blue and red flowers first turn white in the above gaseous mixture, and then reacquire their colour, is connected herewith.

8. *Chlorine, bromine, and iodine.*—When bleached flowers and fruit are suspended in atmospheric air charged with the vapour of chlorine, iodine, or bromine, they reassume their colour as in ozoniferous air. When left long in such atmospheres, the flowers are again bleached.

9. *Sulphuretted hydrogen* quickly restores the original colour to bleached roses, &c.

10. *Heat.*—When a bleached bluebell, or pink, &c. is suspended in the mouth of a bottle in which water is boiling, the flowers instantly reacquire their colour, but again become white when removed from the steam and allowed to cool. In this manner a flower may be made to appear white and coloured several times in a minute. Frequent immersion of the bleached flowers in the steam, or when left long in it, restores the colours, so that the flowers on cooling do not again become white. An extract of red roses in water containing acetic acid is instantly decolorized by an aqueous solution of sulphurous acid, turns red again on being warmed, and again colourless on cooling. All the reagents enumerated under 1–8 as capable of restoring the colours of flowers and fruit bleached by sulphurous acid, have the property in common of converting that acid into sulphuric acid.

To explain these phænomena, Schönbein adopts the view of Berzelius, that the blue and red pigments of flowers form with sulphurous acid colourless, and with sulphuric acid coloured compounds.—*Journ. für Prakt. Chem.*, vol. liii. p. 321.

Researches on the Telluret of the Oxide of Æthyle.
By J. W. Mallet.

The telluret of the oxide of æthyle, or hydrotelluric æther, is obtained by distilling a concentrated solution of sulphovinate of baryta with telluret of potassium. Prof. Wöhler, who discovered this substance, observed that it dissolves with the assistance of heat in nitric acid, with disengagement of hyponitric acid gas, and that hydrochloric acid poured into this solution precipitates a heavy oleaginous liquid; but he did not determine the nature of the product.

Mr. Mallet undertook to investigate this reaction, and his researches have proved that the telluric æther acts the part of an

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organic radical, capable of combining with the metalloids, and in particular with oxygen, with which it forms a basic oxide. In order to be able to designate these combinations more readily, we shall substitute for telluret of æthyle the expression telluræthyle, which is shorter and more in accordance with the new properties discovered in this body.

Telluræthyle dissolves readily in nitric acid, with disengagement of red vapours; the solution, evaporated at a gentle heat, leaves a white crystalline mass, which is completely soluble in water, and which deflagrates like gunpowder when heated. It is the nitrate of the telluræthylic oxide, $C^4 H^5 TeO, NO^5$. The base of the salt being soluble in water, it cannot be separated by alkalies. Sulphurous acid reduces it quickly, and separates the telluræthyle in dark red drops. Hydrosulphuric acid produces in a solution of the salt an orange precipitate, which melts when the solution is heated into a heavy black liquid, which is the sulphuret of telluræthyle, $C^4 H^5 Te, S$.

The oily colourless liquid, which is precipitated when hydrochloric acid is added to the above nitric solution, is chloride of telluræthyle, $C^4 H^5 Te, Cl$; it has a disagreeable odour; it may be distilled without decomposition, but its boiling-point is somewhat high; by ebullition with water, it distils very slowly.

When oxide of silver is placed in presence of this chloride under water, it is soon decomposed, with disengagement of heat; the oily liquid disappears; the oxide of silver is converted into chloride, and there is left a solution of telluræthylic oxide, which contains neither chlorine nor silver. Evaporated at a gentle heat, it leaves the base in the form of a colourless highly-crystalline substance. Its aqueous solution has an alkaline reaction.

Heat decomposes this base; the tellurium separates, and an oil of an exceedingly disagreeable odour is volatilized. Heated in the air, it burns with a blue flame. Sulphurous acid reduces and precipitates telluræthyle from its solution; hydrochloric acid precipitates the chloride of telluræthyle.

Telluræthylic oxide is likewise formed, but exceedingly slowly, by direct oxidation in contact with the air from telluræthyle, especially when the latter is dissolved in alcohol. It is also obtained in the state of sulphate by treating telluræthyle with dilute sulphuric acid and peroxide of lead. Its solution determines a yellow precipitate in the bichloride of platinum, a white one in the bichloride of mercury. When mixed with a somewhat concentrated solution of chloride of ammonium, it expels ammonia, and gives rise, after some time, to the production of a soluble salt in radiate groups of crystals. The author thinks the composition may be represented by the formula $C^4 H^5 TeCl + 2NH^4 Cl$, but his analyses are too incomplete to admit of this being considered certain.

The author vainly attempted to obtain the telluric mercaptan, $C^4 H^5 Te, HTe$, by distilling a mixture of telluret of potassium and of sulphovinate of baryta dissolved in water, and saturated with tel-

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luret of hydrogen. At the commencement, he obtained only ordinary telluric æther, and towards the end a heavier liquid with a higher boiling-point and a deeper red colour. He regards it as a bitelluret of æthyle, $C^4 H^5 Te^2$.—Liebig's *Annalen*, lxxix. p. 223.

On the Employment of Sulphate of Zinc for the Preservation of Animal Matters. By M. Falconet.

According to the author, the substances the most difficult to preserve, as the brain, the intestines, and other pathological preparations, may be most effectually preserved in a solution of the sulphate of zinc, retaining all their characters without the least alteration, and, what is very important, not experiencing the contraction observed when alcohol is used. The steel instruments employed for operating on the substances which have been injected with the preserving liquid, are not injured even when immersed directly in the liquid, and left there for twenty-four hours.—*Comptes Rendus*, Dec. 1, 1851.

ANALYTICAL CHEMISTRY

On a new Method of detecting the most minute Traces of Iodine and Iodides, and of separating Bromides from Iodine or Iodides. By M. Grange.

In endeavouring to find an easy mode of detecting the presence of iodides in the potable waters, I found a process which I think will prove of great service. The presence of iodide of potassium in any colourless liquid containing about five-millionths of its weight of iodide of potassium can be easily ascertained; it suffices to pour into a test-glass a few grammes of the liquid under examination, to add to it a few drops of solution of starch, and to pass through it a few bubbles of fuming hyponitric acid; the reaction is instantaneous; the liquid acquires a pale rose colour inclining to violet for solutions which contain five-millionths of iodide at the most; and when the experiment is made upon a liquid which contains one hundred-thousandth of its weight of iodide, it takes a bright blue colour. The presence of alkaline salts does not in the least modify the phænomena; as soon as the liquid becomes acid, the reaction is produced. Salts of lime, and especially the chloride and sulphate, slightly modify the reaction; in the latter case the iodide of starch assumes with very minute quantities of iodine, a paler and more violet tint. When the reaction is not very distinct, the liquid should be set aside for a few minutes, when a slight deposit of iodide of starch is formed, indicating the presence of iodine.

The strength of the liquids on which I experimented had been

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fixed with the greatest care; and I mixed, together or separately, all the salts that are generally met with in waters.

Liquids containing one hundred-thousandth of iodide gave a very distinct reaction, a brilliant blue colour.

Liquids containing five-millionths of iodide are coloured violet-rose.

Liquids containing one-millionth and less do not furnish a satisfactory result. In such case I have recourse to the method suggested by M. Rabourdin, the use of chloroform. After having passed a current of hyponitric acid into the liquid under examination, or nitric acid containing a large quantity of hyponitric acid in solution, a small quantity of iodide of potassium is poured into it, which acquires a red colour, when by agitating the liquid the greater portion of the iodine liberated has been dissolved in the chloroform.

The chloroform acquires a red and violet colour when it contains in solution a small quantity of iodine, and orange when it contains a small quantity of bromine. When a powerful acid is used, nitric or ordinary sulphuric acid, the bromides are partially decomposed, and colour the chloroform. Under this circumstance, it would not be possible to detect the presence of a very minute quantity of iodine; in such case a few drops of a solution of potash are mixed with the chloroform, which reacquires its proper colour; it is then decanted, and the characteristic reaction with a solution of starch obtained by means of a few bubbles of hyponitric acid as soon as the liquid has become acid.

It is very easy by this method to detect the presence of iodide of potassium in waters which do not contain more than one ten-millionth of their weight of it. I have ascertained directly, and without evaporation, the presence of iodide of potassium or sodium in running waters, even in those of the Seine, by washing 1 litre of acidulated water with a small quantity of chloroform.

It is easy to separate the most minute trace of iodide from solutions containing bromides by the action of hyponitric acid, the iodide alone being decomposed. In the same manner as hyponitric acid serves to detect iodine, the iodide of potassium may be used as a test for nitrites by means of a solution of starch and a few drops of water acidulated with hydrochloric acid.

Whenever organic substances have to be examined, or liquids coloured by organic substances, it is necessary to destroy them by incineration with a little potash; the iodide of potassium is extracted from the ash with a little water.

When the liquid, after evaporation of a certain quantity of water, does not contain at least one-fourth of a milligramme of iodine, and this latter case is very rare, the determination of the quantity by the balance is impossible. We are compelled to compare the reactions with one another; but the results, obtained by employing the most minute precautions, can only be considered as satisfactory approximations.—*Comptes Rendus*, Dec. 1, 1851.

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THE CHEMICAL GAZETTE.

No. CCXXII.—January 15, 1852.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Examination of the Root of Madder, Rubia tinctorum. *By* Prof. ROCHLEDER.

THE root examined by the author was imported from Smyrna by way of Vienna; it consisted of pieces several inches in length, the external appearance of which showed that it had not been submitted to any artificial treatment.

The root, cut up into small pieces, was conveyed gradually, and in small quantities at a time, into boiling water. In this manner a reddish-yellow liquid is obtained, which is separated from the pieces of root by being passed through a fine sieve.

When mixed with a solution of neutral acetate of lead in water, this decoction furnishes a violet precipitate, which quickly separates from the hot liquid. The supernatant liquid has a golden-yellow colour in thin layers, but appears reddish-yellow in large masses.

When cold, the precipitate is brought on a filter, and washed with cold water; it contains the whole of the alizarine and purpurine, some fat, citric acid, with traces of ruberythric acid and rubichloric acid, and also sulphuric and phosphoric acids in combination with oxide of lead.

Citric Acid.—When the above-mentioned violet precipitate is formed into a paste with water, a current of sulphuretted hydrogen passed through it, and the sulphuret of lead brought upon a filter, a very pale yellow liquid passes through, which contains the sulphuric, phosphoric, citric, traces of ruberythric and rubichloric acids; the fat, alizarine and purpurine remain with the sulphuret of lead.

After removing the sulphuretted hydrogen by a gentle heat, the liquid is divided into three equal portions. The first portion is precipitated with neutral acetate of lead, the other two portions added, and left for twenty-four hours in a moderately-warm place, being frequently stirred. The precipitate is collected upon a filter; it contains only a little citrate of lead, much sulphate, and some phosphate; the liquid contains free acetic acid, much citric acid, and some oxide of lead. The liquid is completely precipitated by basic acetate of lead, the precipitate collected on a filter, suspended in

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water, and sulphuretted hydrogen passed through it. The solution, filtered from the sulphuret of lead, is evaporated *in vacuo* over sulphuric acid until it is of the consistence of a syrup; it is then left exposed to the air some days in a dish covered with paper, when it becomes filled with granular crystals of an agreeable acid taste.

A solution of these crystals in water is colourless, gives no precipitate with nitrate of silver, but a white one on the addition of ammonia. Lime-water determines no precipitate, which is also the case with a dilute solution of chloride of calcium; on the addition of ammonia a slight turbidness results; and if the whole be boiled, a copious precipitate of citrate of lime falls. A solution of neutral acetate of lead produces a bulky white precipitate. Persalts of iron cause no precipitate; on the contrary, the acid prevents the precipitation of the peroxide of iron by ammonia. These reactions, as also the deportment of the acid on being heated, are characteristic of citric acid. An analysis of the acid and of two lead salts gave—

Carbon	37·55	12 =	37·50
Hydrogen	4·54	8	4·17
Oxygen	57·91	14	58·33

The oxalic acid stated to exist in madder by Schunck, the malic acid found by Kuhlmann, as also the tartaric acid mentioned by others, could not be detected in the madder examined.

Alizarine and Purpurine.—When the sulphuret of lead, which is formed when the violet precipitate produced in the madder decoction by a solution of acetate of lead is decomposed under water with sulphuretted hydrogen, is exhausted with boiling alcohol, a dark brownish-yellow solution is obtained, which contains fat, alizarine and purpurine. When mixed with water, it becomes turbid; and on the addition of more water, a yellow jelly results, which shrinks into flakes consisting of alizarine and some fat mixed with a little purpurine, while the greater portion of the latter has remained dissolved in the weak alcohol.

When the separated flakes are dried, rubbed to a powder, and washed upon a filter with cold æther, the latter passes through of a brown colour, and leaves on evaporation a fat, contaminated with some alizarine, of a brown colour, and the consistence of hog's lard. The washed alizarine was dissolved in boiling æther, and this allowed to evaporate spontaneously in a tall glass loosely covered with paper; the alizarine crystallizes in shining orange-coloured plates. Dried at 212° for thirty-six hours, it exhibited the following composition:—

Carbon.....	67·93	60 =	4500·0	67·80
Hydrogen	3·77	19	237·5	3·58
Oxygen	28·30	19	1900·0	28·62

The amount of purpurine in the madder examined was exceedingly small in comparison with that of the alizarine, and scarcely amounted to three-fourths of a gramme for 25 lbs. of the root. Alizarine can be separated from the purpurine by dissolving the mixture of the two bodies in a solution of caustic potash, and mix-

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ing the solution with one of protosulphate of iron, and setting the mixture aside in a closed vessel. A nearly black precipitate is obtained, above which is a dirty brownish solution, which instantly turns blood-red in contact with the air. Hydrochloric acid precipitates purpurine from it in flakes.

From this we see that purpurine may be reduced like indigo, and again regenerated by the absorption of oxygen from the air. At the same time the liquid gives off the odour of an indigo-bath.

As above stated, the aqueous decoction of the root furnishes a violet precipitate with a solution of neutral acetate of lead. The liquid filtered from it, on being mixed with a solution of tribasic acetate of lead, yields a precipitate which is readily soluble in an excess of the precipitant, is of a dark flesh, almost brick-red colour, and consists of ruberythric acid, rubichloric acid, and small quantities of citric and phosphoric acid combined with oxide of lead. The chief product is ruberythrate of lead.

Ruberythric Acid, $C^{72}\ H^{40}\ O^{40}$.—The precipitate just mentioned is diffused in water, and a current of sulphuretted hydrogen sent through it. As soon as the decomposition is complete, the mass is poured upon a filter, and then washed with a little cold water. The liquid which passes contains some phosphoric, citric and rubichloric acids. Small traces of the ruberythric acid impart a yellow colour to it. The principal portion of the last-mentioned acid is retained by the sulphuret of lead.

When the sulphuret of lead is repeatedly exhausted with boiling alcohol, the filtered yellow solution evaporated in the water-bath until two-thirds of the alcohol are expelled, then mixed with water and an aqueous solution of hydrate of baryta, a small quantity of a white precipitate forms, which is separated by filtration. On the further addition of barytic water, ruberythrate of baryta separates in dark cherry-red flakes, which are collected on a filter. The filter, together with the precipitate, is placed in a beaker, and treated with dilute acetic acid. The precipitate dissolves with a yellow colour, except a small quantity of a brown viscous matter, which is separated. The acetic solution is nearly neutralized with ammonia, and mixed with a solution of tribasic acetate of lead. A vermilion-coloured lead salt forms, which is washed with water, to which some alcohol has been added. The washed precipitate is suspended in alcohol, and sulphuretted hydrogen passed through it, the liquid containing the suspended sulphuret of lead is heated to boiling, and filtered hot. On evaporating the golden-coloured solution, light yellow crystals separate, the quantity of which increases as the liquid cools.

These crystals are the ruberythric acid. They are pressed between blotting-paper, dissolved in the smallest requisite quantity of boiling water, and the boiling-hot filtered solution allowed to cool slowly. The acid separates in silky yellow prisms, which gradually fill the whole liquid; they are placed upon folds of blotting-paper to absorb the mother-liquor, and then dried *in vacuo* over sulphuric acid. On analysis they gave—

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Carbon.....	54·54	72	= 5400·0	54·54
Hydrogen	5·16	40	500·0	5·05
Oxygen	40·30	40	4000·0	40·41

Ruberythric acid dissolves with difficulty in cold, readily in hot water, in alcohol and æther, with a golden-yellow colour; in aqueous solutions of the alkalies, with a dark blood-red colour. Barytic water precipitates the aqueous solution of the acid in dark cherry-red bulky flakes; basic acetate of lead gives a vermilion-coloured precipitate. An aqueous solution of the acid, mixed with a solution of alum, is decolorized upon the addition of ammonia, and furnishes a precipitate, which, after being washed, dried at 212°, and reduced to powder, forms a lake which in brilliancy and intensity of colour is not inferior to Chinese vermilion.

An aqueous solution of the acid, to which a little alcohol had been added, was mixed with basic acetate of lead, heated to boiling, and the cinnabar-red precipitate washed with water containing alcohol. Dried *in vacuo* over sulphuric acid, it furnished on analysis the following results:—

Carbon.....	22·74	72	= 5400·0	22·97
Hydrogen	2·00	37	462·5	1·96
Oxygen	15·82	37	3700·0	15·75
Oxide of lead ..	59·44	10	13945·0	59·32

3 equivs. of water have therefore been eliminated, and 10 equivs. of oxide of lead assimilated.

When ruberythric acid is heated to boiling with an aqueous solution of perchloride of iron, it dissolves with a dark brownish-red colour. On cooling, the solution remains clear; it turns yellow on the addition of hydrochloric acid, and deposits the acid in yellow flakes.

As already stated, ruberythric acid dissolves with a blood-red colour in aqueous solutions of the caustic alkalies. When such a solution, containing an excess of potash, is heated to boiling, the blood-red colour of the solution suddenly changes into that of an alkaline solution of alizarine, *i. e.* purple by transmitted, violet-blue by reflected light. Upon the addition of an acid, the liquid is decolorized, with separation of bulky bright orange flakes of alizarine.

An aqueous solution of ruberythric acid, mixed with hydrochloric acid, becomes somewhat of a paler yellow, turbid when heated, and when the ebullition has lasted one minute, the liquid is converted into a yellow jelly, which shrinks into flakes consisting of pure alizarine.

In order to ascertain what takes place in this reaction, a large quantity of ruberythric acid was boiled with hydrochloric acid and water, the separated flakes collected upon a filter after twenty-four hours, washed with water, and dried at 212°. They furnished the composition of anhydrous alizarine. A mixture of hydrated oxide of lead and carbonate of lead was added to the filtered liquid as long as any effervescence was perceptible; the liquid filtered from the lead salts evaporated on the water-bath, mixed with some sulphu-

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retted hydrogen and some water, separated from a trace of sulphuret of lead, and evaporated on the water-bath. A syrupy residue was left, which burnt upon platinum foil with the odour of sugar, and yielded with a solution of sulphate of copper and caustic potash a blue liquid, which was decolorized on being heated, with separation of protoxide of copper. The process may be explained in the following manner:—

$$C^{72}H^{40}O^{40}, \text{ ruberythric acid} = C^{12}H^{10}O^{10}, \text{ sugar} + C^{60}H^{30}O^{30}, \text{ alizarine.}$$

Ruberythric acid is consequently a perfectly analogous substance to caincic acid, a conjugate compound of a hydrocarbon, which is resolved by acids and alkalies at a high temperature into sugar and alizarine, just as caincic acid under similar circumstances splits up into sugar and kinovic acid. The alizarine and the sugar (part of the latter at least) of the madder root originate from the ruberythric acid by decomposition. The microscopic investigations of Decaisne, which led him to conclude that the red colouring matters of the root were formed from a yellow substance, are hence completely confirmed and explained. Mr. Higgin was equally led from some experiments to suspect such to be the case*.

Ruberythric acid, more or less contaminated with other substances, had already been observed by several chemists, and received various names. It is the madder-yellow of Runge, the xanthine of Kuhlmann, Schunck and Higgin. Higgin's xanthine is the purest. The statements of some chemists, that xanthine has a sweet or bitter taste, gives with sulphuric acid a green precipitate, &c., show that sugar, rubichloric acid, &c. were mixed with it; for in the pure state the acid is tasteless, and rubichloric acid gives with sulphuric acid a green product of decomposition. From the behaviour of ruberythric acid towards acids, we see the advantage of the application of sulphuric acid in the preparation of garancine, garanceux and colorine. The amount of alizarine is considerably increased by the decomposition of the ruberythric acid, and the colouring power of the madder augmented in the same proportion.

Rubichloric Acid.—In the precipitate which basic acetate of lead produces in the decoction of madder which has already been treated with neutral acetate of lead, rubichloric acid is contained along with the above-mentioned substances combined with oxide of lead. The greater portion however of the acid is contained dissolved in the yellow liquid filtered from the precipitate. If this be mixed with ammonia, at first a rosy, and then a white precipitate falls, which consists of ruberythrate, rubichlorate, hexabasic acetate of lead,

* Those who read Mr. Higgin's paper (Phil. Mag., Oct. 1848) will find, from the careful experiments therein detailed, that he did rather more than suspect. In summing up, he writes,—"The foregoing series of experiments warrant us, I think, in drawing the conclusion, that all the colouring matter in madder springs primarily from xanthine, an opinion held by Decaisne, who observed that fresh madder roots contained only a deep yellow fluid;" a conclusion the correctness of which is borne out by the recent researches of Schunck, as well as the present of Prof. Rochleder.—Ed.

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and a compound of oxide of lead with grape-sugar. When suspended in water and decomposed by sulphuretted hydrogen, the ruberythric acid remains for the greater part with the sulphuret of lead, from which it can be obtained, whilst a small portion passes into the liquid, and colours it yellow. Acetic acid, sugar, and rubichloric acid dissolve in water. The liquid filtered from the sulphuret of lead is mixed with pure animal charcoal, and set aside in a warm place in a closed vessel for twenty-four hours, and frequently agitated. The decolorized liquid separated by filtration from the charcoal is mixed with basic acetate of lead, filtered from the slight precipitate produced, and mixed with an ammoniacal solution of acetate of lead. A white precipitate forms containing sugar and rubichloric acid, which becomes dirty yellow on ebullition, absorbs carbonic acid from the atmosphere, and when treated with water containing some ammonia, colours it pale red. It is collected upon a filter, washed with alcohol, suspended in anhydrous alcohol, and decomposed with dry sulphuretted hydrogen. Most of the sugar remains with the sulphuret of lead, but a little of it passes into solution with the rubichloric acid. The colourless alcoholic solution is evaporated *in vacuo* over sulphuric acid and hydrate of potash, and the residue treated with absolute alcohol, which dissolves the rubichloric acid.

This acid is insoluble in æther, readily soluble in alcohol and water, colourless or slightly yellow, owing to incipient decomposition. Its solutions, evaporated in the air on the water-bath, acquire a brownish-yellow colour, and leave a viscous mass. Rubichloric acid has an insipid, somewhat nauseous taste, and no odour. With alkalies it turns yellow, but again becomes colourless upon the addition of an acid. Barytic water and neutral acetate of lead give no precipitate, basic acetate of lead a slight, and ammoniacal acetate of lead a copious white precipitate. A lead salt, prepared as just described, dried *in vacuo*, furnished the following numbers on analysis. There was certainly some hydrated oxide of lead mixed with it. The formula of the acid is $C^{14} H^{8} O^{9}$:—

Carbon.....	13·05	84	= 6300·0	13·01
Hydrogen	1·58	59	737·5	1·52
Oxygen	13·43	65	6500·0	13·44
Oxide of lead ..	71·94	25	34862·5	72·03

Dr. E. Willigk has also detected rubichloric acid in the herbaceous part of the madder-plant, and has examined two of its lead salts.

R. Schwartz found the same acid in *Asperula odorata*. He obtained from a lead salt of this acid the following numbers:—

Carbon	17·56	42	17·51
Hydrogen	2·09	40	2·08
Oxygen	18·27	33	18·37
Oxide of lead.....	62·08	8	62·04

The formula $C^{14} H^{8} O^{9}$ is confirmed by the products of decomposition of this substance by acids at a high temperature. Mixed

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with hydrochloric acid, the mixture, on being heated, turns first blue, then green, and deposits a dark green powder, which dissolves in alkalies with a blood-red colour, acquires a dirty tint on desiccation at 212°, and a violet colour on exposure to the air at the ordinary temperature, with absorption of ammonia, and probably also of oxygen. The author calls this substance chlorrubine. Debus has communicated two analyses of this substance, for which he has calculated the formula $C^{30} H^{14} O^{11}$, for which the author substitutes the formula $C^{60} H^{27} O^{22}$, which agrees perfectly with the analyses of Debus. Analysis I. is by Rochleder, analysis II. by Schwartz; the latter made with chlorrubine from the herb of the madder-plant:—

Carbon.....	63·94	63·67	60	=63·94	61·17	12=61·01
Hydrogen	5·02	4·94	27	4·80	5·07	6 5·08
Oxygen	31·04	31·39	22	31·26	33·76	5 33·91

Analysis I. corresponds to the formula $5(C^{12} H^4 O^3)+7HO$, analysis II. to the formula $C^{12} H^4 O^3+2HO$.

Chlorrubine, prepared by heating in the water-bath a solution of rubichloric acid mixed with hydrochloric acid, and which had separated partly in flakes, and partly on the surface in shining copper-coloured films, when dried *in vacuo* over sulphuric acid, had the following composition, $2(C^{12} H^4 O^3)+HO$:—

Carbon.....	68·61	24	= 1800·0	68·90
Hydrogen	4·39	9	112·5	4·31
Oxygen	27·00	7	700·0	26·79

When the operation is carried on in a retort, an acid water, containing hydrochloric and formic acids, passes over; the distillate, partially neutralized with potash and distilled, yields a liquid which, on being saturated with potash, reduces salts of silver and peroxide of mercury:—

$C^{14} H^8 O^9$, rubichloric acid $= C^2 H^2 O^4 + C^{12} H^4 O^3$, chlorrubine $+2HO$.

Chlorrubine appears more bluish-green, or grass-green, or black-green, according to the time it has been heated and the quantity of hydrochloric acid used; and contains, when dried *in vacuo*, variable quantities of chemically-combined water. The above analysis is that which furnished the least quantity of water. This chlorrubine burns with as much difficulty as fossil coal, even with the use of chromate of lead. Hydrochloric acid produces the same decomposition at the ordinary temperature, only it requires several months to be completed.

Besides alizarine, a very small quantity of purpurine, ruberythric acid, citric acid, sugar and some fat, no other substance was contained in the aqueous decoction of the madder examined; neither Schunck's rubiacine nor his rubiane, α- and β-resin, could be detected. Possibly these substances are products of decomposition, resulting from the use of more powerful reagents, with which the root was treated.

The madder which had been exhausted with boiling water still retained a significant amount of colouring matter, which could be in

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part obtained by exhaustion with boiling alcohol. The root, exhausted with alcohol, furnished, on ebullition with water containing caustic potash, pectic acid, which was separated in brown gelatinous flakes on neutralizing the liquid with hydrochloric acid. By boiling with alcohol, some alizarine could be extracted from the pectic acid.

But even the madder which had been treated with a solution of potash still retained colouring matter. The only means of removing all the pigment from the madder is boiling the root with alcohol containing some sulphuric acid. The compounds of alizarine, insoluble in water, alcohol and alkalies, are decomposed by the sulphuric acid, and the liberated alizarine dissolves in the hot alcohol.

Had the composition of madder and the deportment of its constituents been ever so accurately known, no more advantageous method for procuring the greatest possible amount of alizarine could have been chosen than that employed by Lagier and Thomas for the preparation of colorine. The sulphuric acid decomposes the combinations of alizarine, renders the latter soluble in alcohol, destroys the ruberythric acid, and produces from it a further quantity of alizarine. The alizarine, separated from its compounds and rendered soluble, as also that produced by the decomposition of the ruberythric acid, is extracted by alcohol from the carbonized madder.

The red colour which madder furnishes in dyeing is, according to Rochleder, a double salt of alizarine with alumina and oxide of tin. Pieces of woollen stuff, mordanted with tin salt, placed in a boiling solution of alizarine in a solution of alum to which a little ammonia has been added, are dyed of a beautiful yellow in five minutes. If they are now boiled in water containing a little ammonia, and well rinsed, they are when dry dyed of a Turkey-red. In this process, galls, sumach, chalk, dung, oil, and fatty acids are entirely excluded, and nevertheless the peculiar colour is produced.—*Berichte der Wiener Academie.*

On the Combinations of Carbonic Acid with Oxide of Copper. *By* Prof. H. Rose.

When a solution of sulphate of copper is precipitated from concentrated or dilute cold solutions by carbonate of soda or potash, the precipitate is at first bulky and blue, but becomes more dense and green by long standing and by washing. It has then the composition of native malachite, and consists of equal atoms of neutral carbonate of copper and hydrated oxide of copper, CuO,CO^2+CuO,HO. When, on the other hand, the blue precipitate, without being washed, is pressed between blotting-paper until it no longer moistens it, it retains its blue colour, but still contains alkaline carbonate, which can be removed by water, when the compound also becomes green.

When the solutions of the sulphate of copper and carbonated alkali are mixed and boiled, more carbonic acid is expelled, and the precipitate puts on a brownish-black colour, but at the same time the alkaline sulphate formed is decomposed by the carbonate of copper, and basic sulphate of copper produced. The precipitate

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consequently contains a considerable quantity of sulphuric acid, which cannot be removed by washing with hot water; and the less carbonic acid, the longer the boiling was continued, and the more dilute the solutions employed.

The blue precipitate produced by bicarbonated alkali also becomes green when washed with water, and has the composition of malachite.

The artificial compound CuO, CO^2, CuO, HO may be heated to 302° F. without alteration; but if the temperature be raised to 392°, it begins to decompose slowly, and it takes a long time before the weight remains constant. The residue, which has experienced a loss of 25 per cent. in weight, is of a velvet-black colour, and consists of oxide of copper, still however retaining a small quantity of water, which is held back with great tenacity, and is only expelled at a red heat. The same hydrate of the oxide of copper is formed when oxide of copper is precipitated from its solution by boiling with an excess of hydrate of potash. After being washed, it retains water, which is only expelled at a red heat.

Malachite behaves precisely like the artificial compound, with this sole difference, that the temperature at which it begins to decompose is somewhat higher. At 392° malachite experiences but a very slight loss; at 428°, it begins, although very slowly, to decompose; at 482° it turns brown, and at 572° black. The residue now consists of oxide of copper, but still contains a little water. But whilst malachite can be exposed to a temperature of 392° with scarcely any decomposition, it parts with carbonic acid when the pulverized mineral is boiled with water; it then loses its green colour, becomes dirty green, and subsequently black, at the same time disengaging an abundance of carbonic acid.

Azarite, $2CuO, CO^2 + CuO, HO$, resembles malachite in its deportment at a high temperature, and towards boiling water; in the pulverized state it experiences no loss at 572°, and but a trifling one at 428°–482°. It is only at 572° that it is converted into oxide of copper, which however still retains some water; but if the pulverized mineral be boiled, the water expels the carbonic acid, and the blue colour of the powder gradually turns black. The azurite is however not converted into malachite in this operation. By long treatment with cold water, or with water at 140°–176°, it is not altered.—*Berlin Acad. der Wissen.*, 1851, p. 655.

On the Occurrence of Kreatinine in the Urine of the Horse. *By* N. Sokoloff.

The fresh urine was accurately neutralized with hydrochloric acid and strongly concentrated by evaporation; the hippuric acid separated by hydrochloric acid; the filtered liquid neutralized with milk of lime, evaporated nearly to dryness on the water-bath, the mass then boiled on the water-bath in a flask with alcohol, filtered after cooling, and mixed with chloride of zinc; the precipitate which formed was washed with very dilute alcohol, boiled in water with

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hydrated oxide of lead, and evaporated. Crystallized kreatinine was obtained, which afforded on analysis—

Carbon	36·42	8 =	48	36·64
Nitrogen	..	3	42	32·06
Hydrogen	7·07	9	9	6·87
Oxygen	..	4	32	24·43

Liebig's *Annalen*, lxxviii. p. 243.

On some Compounds of the Cetyle Series. By F. Fridau.

By the action of phosphorus and iodine upon æthal at a temperature exceeding 212°, the protiodide of cetyle, $C^{32} H^{33} I$, is formed; it is an oily substance, and when pure colourless. When bromine is employed instead of iodine, the reaction is more lively, and protobromide of cetyle is formed, a liquid very similar to the iodine compound.

Sodium combines with æthal at 212°, with a brisk disengagement of hydrogen, and forms æthal-sodium. This treated at 212° with an excess of iodide of cetyle is converted, with separation of iodide of sodium, into a substance which solidifies on cooling into a radiate mass, is very readily soluble in æther, much less so in hot, and but sparingly in cold alcohol; it crystallizes from the solutions in shining laminæ, which melt at 131° F., and solidify at 127°. It is the æther of the cetyle series, the oxide of cetyle, $C^{32} H^{33} O$.

By the continued action of dry ammoniacal gas upon the protiodide of cetyle at a temperature exceeding 302°, iodide of ammonium is separated, and a solid substance formed, which melts at 102°, solidifies at 91°, dissolves very readily in æther, with difficulty in boiling alcohol, and separates from the solution on cooling in slender needles. It is perfectly indifferent in its chemical deportment. Its composition corresponds to the formula $C^{96} H^{99} N$, or an ammonia in which the 3 equivs. of hydrogen are replaced by the radical cetyle; its formula is therefore $3(C^{32} H^{33}) N$, and its name tricetylamine.

The substitution of cetyle for 1 or 2 equivs. of the hydrogen of ammonia was not possible.

Aniline acts upon iodide of cetyle at 212°; hydriodate of aniline separates, and two new bases are formed; the one is readily soluble in æther and alcohol, from which it crystallizes on cooling, melts at 108°, and is represented by the formula $C^{46} H^{39} N$. It may be considered as $\left.\begin{matrix} C^{32} H^{33} \\ C^{12} H^{5} \\ H \end{matrix}\right\} N$, or cetylophenylamine.

The muriate is easily soluble in æther and alcohol, from which it separates in white crystalline crusts, which readily acquire a faint reddish tint. The platinum compound dissolves in æther and alcohol; from the latter solution it is precipitated, on the addition of water, in fine crystalline flakes.

The other base is readily soluble in æther, but dissolves with great difficulty even in hot alcohol. The hydrochlorate dissolves

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easily in æther, but the solution appears to decompose rapidly. Its alcoholic solution furnishes, on being mixed with bichloride of platinum, a whitish precipitate, the amount of platinum in which, as also th origin of the base, renders probable the formula $2\left(\begin{matrix}C^{32}H^{33}\\C^{12}H^{5}\end{matrix}\right)N$, which is that of bicetylophenylamin.—Liebig's *Annalen*, October 1851.

Further Observations on Uroxanic Acid. By Dr. STÆDELER.

The author, in calculating the formula for this acid*, had made use of Marchand's tables; he has since found that the logarithm 69791 has been used, instead of 79792, for the amount of nitrogen in ammonio-chloride of platinum, whence the author was led to admit 11·89 instead of 15·87 per cent. of nitrogen in uroxanate of potash; the salt consequently contains 4 and not 3 equivs. nitrogen, and the composition of the crystalline salt must be represented by the formula $2KO+C^{10}H^{8}N^{4}O^{10}+6Aq$:—

Carbon.....	17·20	10 =	750·0	17·03
Hydrogen	3·88	14	175·0	3·98
Nitrogen	15·87	4	700·0	15·90
Oxygen	36·76	16	1600·0	36·34
Potash.....	26·29	2	1177·8	26·75

The water of crystallization amounts to 14·95 per cent.; at 212° the salt lost 14·79. The lead salt dried at 212° contains 52·05 per cent. oxide of lead, corresponding to the formula $2HO+C^{10}H^{8}N^{4}O^{10}$:—

Oxide of lead	52·05	2 =	2789·2	52·24
Anhydrous acid.....	47·95	1	2550·0	47·76

Uroxanic acid has the formula $2HO+C^{10}H^{8}N^{4}O^{10}$:—

Carbon	26·89	10 =	750	27·03
Hydrogen	4·17	10	125	4·50
Nitrogen.....	..	4	700	25·23
Oxygen	..	12	1200	43·24

As the comparison shows, $\frac{3}{10}$ths per cent. less hydrogen was found than required by the formula. This difference exceeds by far the limits of an error of observation, and it is therefore highly probable that the acid analysed was mixed with some product of decomposition. As is known, uroxanic acid is decomposed on heating its aqueous solution, with disengagement of carbonic acid. It is scarcely necessary to make a new analysis in order to confirm the formula, as the composition of the salts places it beyond all doubt. Uroxanic acid originates from uric acid simply by the assimilation of 6 atoms of water, $2HO+C^{10}H^{2}N^{4}O^{4}$, uric acid, $+6Aq=2HO+C^{10}H^{8}N^{4}O^{10}$, uroxanic acid.

The derivation of the urea, lantanuric and formic acids, which are formed simultaneously with the uroxanic acid, is explained by

* Chem. Gaz., vol. ix. p. 301.

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the proposed formula; they are produced from the uroxanic acid by the assimilation of 1 atom of water, $2HO + C^{10} H^8 N^4 O^{10}$, uroxanic acid $+ Aq = C^2 H^4 N^2 O^3$, urea, $+ HO$, $C^6 H^4 N^2 O^5$, lantanuric acid, $+ HO$, $C^2 HO^3$, formic acid.

The production of the oxalic acid remains alone unexplained; it must be viewed as resulting from a further decomposition connected with the observed disengagement of ammonia.

Lastly, as regards the substance which the author described under the name uroxile, it agrees very well in composition with that of the anhydrous uroxanic acid, $= C^{10} H^8 N^4 O^{10}$; but the 2 atoms of water amount only to 8·11 per cent., whilst uroxanic acid, according to a more recent experiment, loses 34·84 per cent. at 266°; consequently it must have certainly lost nitrogen at this temperature, probably in the form of cyanide of ammonium or carbonate of ammonia; and the coincidence of the hydrogen and carbon in uroxile with anhydrous uroxanic acid is merely accidental. —Liebig's *Annalen*, lxxx. p. 119.

On a new Source for obtaining Capric Acid, and Remarks on some of its Salts. *By* Mr. Thomas Henry Rowney, F.C.S.*

The following examination of capric acid and some of its salts was made in the laboratory of Dr. T. Anderson, to whom I am much indebted for his kindness in procuring for me the materials to work upon, and also for advice during the progress of this investigation. Capric acid has been found by Chevreul and Lerch† in the butter of the cow and goat; by Redtenbacher‡, amongst the volatile oily acids he obtained by acting on oleic acid with nitric acid; by Gerhardt and Cahours§, by the action of nitric acid on the oil of rue; and by Görgey‖, in cocoa-nut oil. From all these sources it has been obtained only in small quantities, and always along with other acids of the series to which capric acid belongs.

In the present paper I have to point out a new source for obtaining it, namely the fusel-oil or grain-oil of the Scotch distilleries. The principal constituents of grain-oil are water, alcohol, and the hydrated oxide of amyle. The proportions of these constituents vary in the oils obtained from different distilleries; in some cases it is soluble in water, and then consists chiefly of water and alcohol, with a small quantity of the hydrated oxide of amyle; generally it is an oily liquid, lighter than, and insoluble in water. Besides the three above-mentioned constituents, other compounds have been found in it in small quantities. Mulder¶ found œnanthic acid, and Kolbe** found margaric acid. In the oil examined by myself an acid was found, which analysis proved to be capric acid. In what state it exists in the oil I am not able to say, but I think it most probable that it is in combination with the hydrated oxide of amyle.

* From the Transactions of the Royal Society of Edinburgh, having been read March 17, 1851.

† Chem. Gaz., vol. ii. p. 377. ‡ Journal of the Chemical Society, part xix.

§ Chem. Gaz., vol. vi. p. 487. ‖ Chem. Gaz., vol. vii. p. 81.

¶ Liebig's Annalen, vol. xxiv. p. 248. ** Liebig's Annalen, vol. xli. p. 35.

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To obtain the capric acid, the grain-oil was distilled with a thermometer placed in the tubulure of the retort, and the distillate collected in separate receivers. The first portion consisted of water, alcohol and the hydrated oxide of amyle; the second portion was the hydrated oxide of amyle, and a dark-coloured residue was left. This residue was oily; it had a very disagreeable smell, and was insoluble in water and carbonate of potash, even when boiled with a solution of the latter; when boiled with a strong solution of caustic potash, it is rendered soluble in water. Whilst boiling, a strong smell of the hydrated oxide of amyle is given off; and if the operation be performed in a retort with a receiver attached, this compound is found floating on the water that passes over during the operation. It is also rendered soluble by being digested with a strong solution of caustic potash for two or three days on the sand-bath. On adding hydrochloric or sulphuric acid to the cold alkaline solution, a dark oily mass rises to the surface; this was filtered and washed with cold water. I found that the best way to obtain the acid pure was to dissolve it in a dilute solution of ammonia, and then to add chloride of barium until it ceased to give a precipitate; this precipitate was filtered and washed with cold water, then dissolved by boiling with water, filtering whilst hot, and allowing the filtrate to crystallize. It is sometimes dissolved with difficulty by boiling water, owing to its forming hard soapy masses during the boiling; by crystallizing the baryta salt two or three times, it becomes nearly colourless. It was then decomposed by boiling with carbonate of soda, and filtered from the precipitated carbonate of baryta; dilute sulphuric acid was added to the filtrate to separate the capric acid, and by these means it was obtained nearly colourless and in a solid state. To obtain it perfectly pure, it was dissolved in alcohol, and a large quantity of water was added to the alcoholic solution; the mixture becomes turbid, and after standing for some hours, capric acid crystallizes out; and by repeating this process, it may be obtained perfectly pure and colourless. The mother-liquors from the baryta salt were concentrated by evaporation, and then boiled with carbonate of soda, filtered from the carbonate of baryta, and the filtrate decomposed by sulphuric acid. The capric acid obtained from this portion was mixed with a small quantity of an oily acid; the quantity was so small that I was not able to ascertain its constitution.

Capric Acid.—As obtained in the manner I have described, it is a solid, white, and crystalline compound, having a faint odour, and fuses readily when taken between the fingers. It is very soluble in cold æther and alcohol, and does not crystallize from these solutions. It is insoluble in cold water, but dissolves sparingly in boiling water, and crystallizes from this solution on cooling in the form of scales. It is also soluble without decomposition when boiled with concentrated nitric acid, and is precipitated from this solution by the addition of water. It is obtained in a mass of needle-shaped crystals by the addition of water to the alcoholic solution. Its specific gravity is far less than that of water. The crystallized acid commences to fuse at 81° F., and the mercury of the thermometer

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continues to rise to about 116° F. before the whole is completely fused. When allowed to cool, it becomes solid at 81° F. The fused acid is slightly coloured, and has a faint smell; it becomes crystalline on cooling. This fusing-point differs from that generally given. Görgey gives it at 86° F., and others have stated it to be from 60° to 66° F. These differences probably arise from impure acids having been used. For analysis, the crystallized acid, dried *in vacuo* over sulphuric acid, was employed. It furnished:—

Carbon	69·35	69·38	20 =	120	69·76
Hydrogen	11·61	11·65	20	20	11·62
Oxygen	..	..	4	32	18·62

Caprate of Silver.—This salt is formed when AgO, NO^5 is added to a slightly ammoniacal solution of capric acid. It is insoluble in cold water, sparingly soluble in boiling water, and is deposited again on cooling in needle-shaped crystals. It is more soluble in boiling alcohol, but the solution becomes dark-coloured, and the crystals deposited from it are also dark-coloured. Görgey also observed this change. It is very soluble in ammonia, and if the ammoniacal solution be kept in a warm place, so as to drive off the ammonia, a crystalline salt is obtained; but not not having a sufficient quantity, no examination of this compound was made. The silver salt whilst moist is rapidly blackened if exposed to bright daylight; but after drying it may be exposed to the light without undergoing any change. The silver salt for analysis was precipitated and washed during the evening, dried *in vacuo* over sulphuric acid, the receiver being covered with a cloth to prevent the access of light to it; it was then dried in a water-bath at 212° F. It gave:—

Carbon	42·52	42·34	..	20 =	120	43·01
Hydrogen ..	6·81	6·73	..	19	19	6·81
Oxygen	..	..	..	4	32	11·47
Silver	38·27	38·52	38·67	1	108	38·71

Caprate of Baryta was obtained by adding chloride of barium to an ammoniacal solution of capric acid; the precipitate was filtered and washed with cold water. It is soluble both in water and alcohol when boiled with these liquids, and crystallizes out from these solutions on cooling either in needle-shaped or prismatic crystals; the crystals obtained from the alcoholic solution are sometimes of considerable size. This, as also the other salts of the alkaline earths, and the silver salt, are insoluble in water after having been dried, as they float on the surface of the water and repel it; but by first moistening the salt with alcohol, they may be again rendered soluble in boiling water. They are also very difficult to powder and mix for analysis.

The salt analysed was crystallized from water, and dried in the water-bath at 212° F. The baryta was determined as BaO, SO^3, and the combustion was made with chromate of lead:—

Carbon.....	49·88	49·58	20 =	120	50·08
Hydrogen	8·06	8·24	19	19	7·93
Oxygen	..	..	3	24	10·02
Baryta	31·65	31·88	1	76·6	41·97

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Caprates of Lime and Magnesia.—These salts crystallize, and have similar properties to the baryta salt, but they are more soluble both in alcohol and boiling water. No analysis was made of the limesalt, but the base of the magnesia salt was determined. The salt employed for this purpose was crystallized from water, and dried at 212° F. The magnesia was determined as $2MgO, PO^5$. It furnished 11·37 per cent. MgO; the formula $C^{20} H^{19} O^3$, MgO requires 11·25.

I endeavoured to obtain some other salts of capric acid; but as only the salts of the alkaline earths are readily crystallizable, I did not succeed in doing so. The salts I tried were the soda, copper and lead salts. The copper salt is insoluble in water and alcohol, but soluble in ammonia. The analyses of these salts always gave an excess of base; this was caused by my not being able to obtain a neutral ammoniacal salt of capric acid. The lead salt is insoluble in water, and very sparingly soluble in boiling alcohol. The solution on cooling deposits the lead salt in rounded grains.

The soda salt is exceedingly soluble both in cold water and alcohol, and does not crystallize from these solutions. When evaporated to dryness, it dries up to a horny mass, partially crystalline on the surface. It is soluble in absolute alcohol when warmed, and the solution, when allowed to cool, becomes an opalescent mass. I could not obtain it free from NaO, CO^2, even by means of absolute alcohol; consequently the analysis gave an excess of base.

From the analyses made of the soda and copper salts, they appear to be neutral salts; the formula of the soda salt being $NaO, C^{20} H^{19} O^3$, that of the copper salt being $CuO, C^{20} H^{19} O^3$.

Capric Æther was obtained by dissolving capric acid in absolute alcohol, and passing dry hydrochloric acid gas into the solution to saturation. The addition of water to the solution caused the capric æther to rise to the surface as an oily liquid. It was separated from the acid liquid and washed with cold water, and then dried by digesting it with fused Ca, Cl; its specific gravity is 0·862. It is insoluble in cold water, but readily soluble in alcohol and æther.

As the quantity of the æther was too small to allow of an analysis of it being made, I converted it into the following compound:—

Capramide.—The capric æther was dissolved in alcohol, and a strong solution of ammonia was added to it in a stoppered bottle; after a few days the solution became turbid; this turbidity increased after allowing it to stand for a longer period, and crystals began to make their appearance. The digestion was continued until the whole of the æther had disappeared. The crystals were then filtered off, and the filtrate evaporated to dryness on a water-bath; the residue was dissolved in alcohol, and the addition of water caused the capramide to crystallize from the solution; the whole was dissolved in warm dilute alcohol, and allowed to crystallize. As obtained in this manner, it is quite colourless, and crystallizes in brilliant scales, which when dry have a bright silvery lustre. It fuses below 212° F., and is insoluble in water and ammonia. It is very soluble in cold alcohol, and in dilute alcohol when warmed in it.

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Its other properties I could not examine, as I had only sufficient substance for one combustion. For analysis, it was dried *in vacuo* over sulphuric acid, and the combustion was made with oxide of copper; it furnished C 70·62, H 12·17. These numbers correspond to the formula $C^{20} H^{21} O^2 N$, which requires C 70·17, H 12·28.

Observations on Narcotine. *By* M. Wertheim.

The author has continued his researches on narcotine, and has arrived at the conclusion, that opium contains, beside the narcotine of Blyth, two other bases homologous with it. They are both obtained in the same manner as narcotine from opium.

These two bases form a series with narcotine, and this again has so many connected members among the products of decomposition, that it is evident that Blyth's narcotine should be called æthylo-narcotine, and the other two methylo- and propylonarcotine, as follows:—

Methylonarcotine.....	$=C^{44} H^{23} NO^{14}$
Æthylonarcotine (narcotine of Blyth)..	$=C^{46} H^{25} NO^{14}$
Propylonarcotine	$=C^{48} H^{27} NO^{14}$

Methylonarcotine yields, when treated with potash at 392° F., methylamine. With sulphuric acid and manganese, it furnishes, besides a considerable amount of opianic acid, as large a quantity of a base which is represented by the formula $C^{24} H^{13} NO^6$. Precipitated with an excess of mercury, this base gives a salt corresponding in composition to the formula $C^{24} H^{13} NO^6 + ClH + 2HgCl$. Both the base and the mercurial salt resemble Wöhler's cotarnine and cotarnine-perchloride of mercury. The analytical results however differ considerably from the approximative formula given by Wöhler for cotarnine, and they differ nearly as much from the numbers which Blyth obtained for this base. Probably, however, these differences arise from the circumstance that a distinct cotarnine corresponds to each of the three homologous bases. There probably exists therefore a methylocotarnine, $C^{24} H^{13} NO^6$, an æthylocotarnine, $C^{26} H^{16} NO^6$, and a propylocotarnine, $C^{28} H^{17} NO^6$.

Æthylonarcotine the author has not yet examined, but Blyth's narcotine will undoubtedly prove to be such, and will furnish æthylamine.

Propylonarcotine is the base which the author in his former investigation took for Blyth's narcotine. The product of decomposition with potash at 392° F. is propylamine, which the author formerly called œnylamine.

With respect to the assumption of the above-mentioned cotarnine series, the opianine discovered by Hinterberger is greatly in its favour; for if narcotine is the neutral compound of cotarnine with an electro-negative group, and narcogenine the corresponding bibasic compound, then opianine may be regarded as the corresponding binacid compound. The formula of opianine is $C^{66} H^{36} NO^{23}$; that of narcogenine, according to Blyth, is $C^{36} H^{19} NO^{10}$. The results of Blyth's analyses however agree better with the formula

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$C^{36}H^{20}NO^{10}$; and if the equivalent of narcogenine be doubled in accordance with the view above expressed, we have for it the formula $C^{72}H^{40}N^2O^{20}$. If we now admit for æthylocotarnine the expression $C^{26}H^{15}NO^6$, we have—

Opianine, $C^{66}H^{36}NO^{23} = C^{20}H^{11}O^9 + C^{20}H^{10}O^8 + (C^{26}H^{15}NO^6)$
Æthylonarcotine, $C^{46}H^{25}NO^{14} = C^{20}H^{10}O^8 + (C^{26}H^{15}NO^6)$
Narcogenine, $C^{72}H^{40}N^2O^{20} = C^{20}H^{10}O^8 + 2(C^{26}H^{15}NO^6)$.

Journ. für Prakt. Chem., vol. liii. p. 431.

On the Determination of the Equivalent of Phosphorus. *By* Prof. SCHRŒTTER.

The author has endeavoured to determine the equivalent of phosphorus by ascertaining the amount of phosphoric acid produced by the combustion of this substance in a current of perfectly dry oxygen. He employed for this purpose the amorphous red phosphorus, as obtained by the long-continued action of a high temperature upon ordinary phosphorus: this modification, experiencing no alteration from exposure to the air, is capable of being weighed off accurately.

Ten experiments, all agreeing perfectly with one another, furnished as the mean for 1 part of phosphorus, 2·2892 phosphoric acid, whence he deduced for the equivalent of phosphorus the number 387·84. The greatest differences were between 388·25 and 386·70.

Assuming the equivalent of hydrogen as unit, that of phosphorus will be expressed by 31·027. Taking into consideration the possible errors in such a determination, it is evident that the equivalent of phosphorus may be considered as an exact multiple of that of hydrogen, 31.

These results likewise prove that the equivalent adopted by Berzelius, 392, came closer to the truth than the number 400, more recently proposed by M. Pelouze.—*Journ. für Prakt. Chem.*, liii. p. 435.

On a new Test for Urea. *By* Prof. LIEBIG.

When a solution of pure urea is rendered strongly alkaline with solution of caustic potash, and a solution of corrosive sublimate added to it by degrees, a dazzling white precipitate—a combination of the peroxide of mercury with urea—is obtained.

As is well known, a dilute aqueous solution of corrosive sublimate may be mixed with an excess of a solution of bicarbonate of potash without the immediate production of a precipitate; if a solution of urea be added to this mixture, the above-mentioned white precipitate of urea and peroxide of mercury is immediately formed. This compound is so little soluble in water, that by this process $\frac{1}{5000}$th urea can be detected with certainty in a liquid. The whole of the urea can be precipitated from urine by this means, and its application

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to the quantitative determination of urea in animal fluids is evident. I shall take an early opportunity of describing a suitable method for this purpose.

When oxide of silver (recently precipitated is best) is placed in an aqueous solution of urea, it is converted, in the course of a few hours, more quickly when gently heated, into a gray or yellowish-gray granular powder, which appears under the microscope to consist of transparent crystals. This compound when dry gives off ammonia when heated, leaving cyanate of silver, which burns at a higher temperature into sesquicyanide of silver, and finally into pure silver.—Liebig's *Annalen*, October 1851.

On some new Constituents in the Ergot of Rye.
By Dr. F. L. Winckler.

In the analysis of ergotine, prepared by exhausting the ergot of rye with distilled water, and treating the aqueous extract with alcohol, &c., I have discovered in combination with an acid a volatile alkaloid, which is very similar to, if not identical with coniine. It is to this alkaloid that the ergot of rye appears to owe principally its effectiveness, and not, as has hitherto been admitted, to ergotine. Besides this alkaloid, I have found as constituents of ergotine an exceedingly small quantity of kinovic acid, formiates and chloride of potassium.—*Pharm. Cent.-Blatt*, Oct. 1, 1851.

Combustion by Peroxide of Barium.

According to Prof. Wöhler, when small fragments of peroxide of barium are heated in a somewhat capacious glass bulb in a rapid current of carbonic oxide, the peroxide becomes incandescent, and little white flames appear at its surface. A more brilliant phænomenon of combustion, and which is well adapted for a class-experiment, is exhibited on burning the peroxide in sulphurous acid gas. —Liebig's *Annalen*, lxxviii. p. 125.

PATENT.

Patent granted to Robert and John Oxland, *for Improvements in the Manufacture and Refining of Sugar.*

This invention consists in the use of phosphoric acid in a combined state for defecating saccharine liquids, or solutions of sugar, and removing the colour of the same.

On the 26th of April 1849, the present patentees obtained a patent for defecating and removing the colour from solutions of sugar by the employment of acetate of alumina *. In the specification of such patent, lime was directed to be used for effecting the separation of

* Chem. Gaz., vol. vii. p. 455.

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the alumina; but it has been found, that, even when great care is observed, some alumina is liable to be left in solution. When acetate of alumina and lime have been used, the patentees effect the removal of the remaining alumina by the use of superphosphate of alumina or superphosphate of lime, by simply adding a small quantity of either of these substances to the syrup after the completion of the process with acetate of alumina, as described in the former specification; then boiling for two or three minutes, carefully neutralizing the excess of acid by the addition of aluminate of lime, saccharate of lime, lime-water or milk of lime; and when it has been ascertained that the alumina is completely separated, completing the process in the manner described in the former specification.

In place of using acetate of alumina, either alone or combined with phosphoric acid, as above explained, phosphates may be employed directly; and they are capable of producing similar effects to those resulting from the use of acetate of alumina, with the advantage that the whole of the agent employed is separated from the saccharine matters. In treating a saccharine liquid, or solution of sugar (say, for example, an ordinary sample of Mauritius sugar), the patentees dissolve it by blowing up with steam in the usual way, but avoiding the use of blood, and adding a soluble phosphate to the water employed. If crystallized phosphate of soda be used, it should be in the proportion of 1½ lb. thereof for each ton of sugar. The saccharine liquid is brought to the boiling-point, any acidity being neutralized with aluminate of lime, saccharate of lime, lime-water, or milk of lime; and then the syrup thus obtained (which will be of the specific gravity of from 25° to 30° Baumé) is passed through the ordinary bag-filters. The sugar is, by this means, thoroughly defecated, the feculent matters being left in the bags, from which the last trace of sugar may be removed by passing clean water through them. The weak solutions obtained in this way may be used for blowing up fresh quantities of raw sugar. As part of the colour is removed from the syrup by the above-described operation, it may be considered sufficient treatment previous to boiling in the vacuum-pan, or otherwise, for crystallization; but a further amount of colour may be removed by the use of from 5 to 8 per cent., or more, of hydrate of alumina (which has been dried at a temperature of 212° F.) diffused through the water used in blowing up the sugar; and by this means the use of animal charcoal will be rendered unnecessary. The residuary alumina left in the filter-bags, after the whole of the saccharine matter has been washed out, may be dried, and the organic matter removed by ignition; and after further washing, to remove any residuary soluble saline substance, it may be employed for manufacturing hydrate or superphosphate of alumina; or, after the first-mentioned washing, previous to ignition, it may be used over again, with the addition of a further quantity of hydrate of alumina.

When superphosphate of alumina is used, it is mixed in solution

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with the water used in blowing up the raw-sugar in the proportion of 6 lbs. of alumina dissolved in phosphoric acid for each ton of sugar; and while the syrup (at from 25° to 30° Baumé) is being brought to the boiling-point, any acidity is neutralized by the addition of aluminate of lime, saccharate of lime, lime-water, or milk of lime. The syrup is then passed through bag-filters, and the clear syrup conducted into the receiver that supplies the vacuum or other boiling-pan. The subsequent operations are the same as in the old plan of working. The matters left in the filter-bags are treated as above described to remove any remaining saccharine matter.

The patentees prepare the superphosphate of alumina by dissolving alumina in phosphoric acid in the following manner:—They burn bones white, grind them to fine powder, and digest the product in sufficient muriatic acid for the solution of the carbonate of lime only; and then they dry the residue, after carefully washing it, to remove every trace of soluble matter. To a given weight of this residue, mixed with enough water to make a thin paste (in a shallow earthenware tank or vessel), they add a quantity of pure sulphuric acid sufficient to combine with nearly all the lime present, *i. e.* all except 2 or 3 per cent., stirring the mixture well and keeping it warm (say above 90° F.) for about twenty-four hours; and after this they lixiviate the mass with water until all the soluble matters are separated from the sulphate of lime. The strong liquors obtained in this way may be used for combining with alumina, and the weak solutions for lixiviating fresh quantities of phosphoric acid in course of manufacture. When alumina is digested in the phosphoric acid, produced in the manner above described, phosphate of alumina, insoluble in water, is first formed; and by dissolving this in a quantity of phosphoric acid sufficient only for that purpose, superphosphate of alumina is obtained, which should be filtered previous to use.

Aluminate of lime is prepared by dissolving alumina in caustic potash or soda, and then, by the addition of lime-water or milk of lime, precipitating aluminate of lime, which is to be carefully washed. When required for use, the patentees diffuse the aluminate of lime through water; and they prefer to employ it instead of saccharate of lime, or milk of lime, or lime-water.

When making sugar from the cane, they defecate the juice with aluminate of lime in the usual way, neutralizing any excess of lime with superphosphate of alumina or superphosphate of lime; then, after filtering and concentrating the filtered liquid to from 25° to 30° Baumé, they treat the syrup with phosphate of soda, in the same manner as described with respect to raw sugars, and after a second filtration they boil in the usual way.

In the manufacture and refining of beet-root sugar, they proceed as above described for cane-sugar, only using a larger quantity of aluminate of lime or of milk of lime in the first defecation.—Sealed May 15, 1851.

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THE CHEMICAL GAZETTE.

No. CCXXIII.—February 2, 1852.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Combinations of the Sesquioxide of Uranium with Acids. *By* A. GIRARD.

It is known that the sulphite of the protoxide of uranium furnishes a green solution in water charged with sulphurous acid, which in contact with the air turns yellow, from the conversion of the protoxide into the sesquioxide of uranium. In repeating, in M. Pelouze's laboratory, the beautiful investigations of MM. Peligot, Ebelmen and Rammelsberg, on the salts of uranium, I was stopped by this fact; and I sought to ascertain whether in this reaction the oxidation bore at first upon the acid or upon the base, or, in other words, whether the sulphurous acid was able to reduce the sesquioxide of uranium or to combine with it.

Sulphurous acid readily unites with the sesquioxide of uranium, forming a compound of considerable stability. When a current of well-washed sulphurous acid is passed into water holding in suspension some hydrated oxide of uranium (U^2O^3, HO), prepared according to Mitscherlich's method, the liquid becomes yellow. When this liquid is left to spontaneous evaporation, it deposits a salt in small yellow prismatic needles. This salt, heated in a tube, gives off water and sulphurous acid, and leaves a residue of oxide of uranium.

To analyse this salt, I treated it with nitric acid until no more red fumes were given off. The sulphurous acid being thus oxidized, I diluted with water and precipitated with nitrate of baryta. The sulphate of baryta gave the weight of the sulphur, and consequently of the sulphurous acid. I then precipitated the filtered liquid with ammonia, and decomposed the uranate by calcination. Four analyses furnished as mean the following numbers:—

Oxide of uranium	67·4	1 =	67·8
Sulphurous acid	16·6	1	16·9
Water	15·7	4	15·3

This sulphite dissolves in an aqueous or alcoholic solution of sulphurous acid; it is precipitated from its solution on being boiled; it is stable at the ordinary temperature, but is decomposed with disengagement of sulphurous acid when heated.

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When a current of sulphurous acid is passed into water holding uranate of ammonia in suspension, it dissolves, and the liquid deposits a mixture of two yellow salts; one is the neutral sulphite, the other the granular subsulphite, which M. Berthier obtained by boiling a salt of uranium with sulphite of ammonia. The liquid sulphurous acid, poured upon hydrated oxide of uranium, has no action upon it.

The composition of this salt, 1 equiv. of acid for 1 of base, affords a further proof that the sesquioxide of uranium acts the part of a protoxide, as shown by M. Peligot.

I imagined it would be interesting, in this point of view, to prepare the pyrophosphate of uranium, as pyrophosphoric acid always takes 2 equivs. of base to 1 of acid in the case of a protoxide. The salt which I obtained, $PO^5, 2(U^2 O^3)$, has exactly the composition which would be assigned to it according to the theory of M. Peligot. When a solution of pyrophosphate of soda is poured into one of nitrate of uranium, a bulky yellow precipitate of pyrophosphate of uranium is obtained, which subsequently assumes a crystalline state, especially if hot solutions have been employed, and which dissolves in an excess of the precipitant.

To analyse this salt, I took a certain weight, dried at 212°, dissolved it in nitric acid, and boiled it with a known weight of tin. According to the process described by M. Reynoso *, the whole of the phosphoric acid was converted into insoluble phosphate of tin, which furnished the weight of the phosphoric acid. I then precipitated the filtered liquid with ammonia. Four analyses gave as the mean—

Oxide of uranium	79·9	2 =	80
Phosphoric acid	19·6	1	20

When dried at 212°, it loses 11 per cent. of water, which corresponds to 5 equivs. Its formula consequently is $PO^5, 2U^2 O^3 + 5HO$. This salt is equally insoluble in water, alcohol and æther; it is soluble in nitric acid; alkalies precipitate it from this solution. When it is quickly precipitated, it has a beautiful yellow colour, and appears under the microscope in the form of minute granular crystals; in the air it effloresces, and turns pale yellow.

Its solubility in an excess of the precipitant distinguishes it from the ordinary phosphate. This reaction may even be employed to distinguish a phosphate from a pyrophosphate. By pouring into the solution one drop of a very dilute solution of nitrate of uranium, a yellow precipitate is formed in the case of a pyrophosphate, which redissolves, whilst that produced by an ordinary phosphate does not dissolve.—*Comptes Rendes*, Jan. 5, 1852.

On the Occurrence of Citric Acid in Richardsonia scabra.
By Prof. Rochleder *and* E. Willigk.

The acid was detected in all parts of the plant. The herbaceous part was cut into small pieces, and boiled with water. The fil-

* Chem. Gaz., vol. ix. p. 418.

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tered brown decoction was mixed with a solution of neutral acetate of lead, which caused a dirty brownish-yellow precipitate; the supernatant liquid was pale sherry-coloured. Mixed with a solution of tribasic acetate of lead, a bright lemon-coloured precipitate is produced, the colour of which arises from the presence of a certain quantity of a lead salt of the tannic acid. It was suspended in alcohol, decomposed by sulphuretted hydrogen, the liquid filtered from the sulphuret of lead, heated until the excess of sulphuretted hydrogen had been expelled, and then mixed with an alcoholic solution of acetate of lead. The precipitate was brought upon a filter, washed with alcohol, then diffused in a large quantity of water, and heated to boiling. A brownish basic salt is left, while the filtered aqueous liquid yields, on the addition of alcohol, a white precipitate in bulky flakes. This was collected on a filter, dried at 212°, and analysed. It furnished—

Carbon.....	16·07	56	= 4200·0	15·88
Hydrogen	1·65	33	412·5	1·56
Oxygen	19·16	51	5100·0	19·28
Oxide of lead	63·12	12	16734·0	63·28

The precipitate has accordingly the formula $C^{56} H^{33} O^{51} + 12PbO = C^{12} H^5 O^{11}, 3PbO, HO + 2(C^{12} H^5 O^{11} \left\{ \begin{matrix} 2PbO \\ HO \end{matrix} \right) + 5(C^4 H^3 O^3, PbO)$.

The above-mentioned grayish-brown precipitate, which acetate of lead produces in the aqueous decoction of the herb, was boiled with dilute acetic acid, the liquid at once filtered from the insoluble portion, again filtered when cool, and mixed with a few drops of ammonia. A bright yellow precipitate was produced, which was diffused in alcohol and decomposed by sulphuretted hydrogen. The liquid filtered from the sulphuret of lead was precipitated with an alcoholic solution of acetate of lead, the precipitate decomposed under water with sulphuretted hydrogen, and the liquid so obtained mixed with an aqueous solution of neutral acetate of lead as long as the precipitate which is formed appears pure white. Dried at 212°, it furnished on analysis—

Carbon.....	14·96	56	= 4200·0	15·21
Hydrogen	1·39	31	387·5	1·40
Oxygen	18·09	49	4900·0	17·74
Oxide of lead	65·56	13	18128·5	65·65

According to this it has the formula $C^{56} H^{31} O^{49} + 13PbO = 2(C^{12} H^5 O^{11}, 3PbO) + C^{12} H^5 O^{11} \left\{ \begin{matrix} 2PbO \\ HO \end{matrix} \right) + 5(C^4 H^3 O^3, PbO)$.

The *root* of this plant was cut into pieces and exhausted with alcohol. The slightly-coloured infusion was filtered, and precipitated with an alcoholic solution of acetate of lead, the precipitate decomposed by sulphuretted hydrogen under water, the liquid filtered from the sulphuret of lead, and after expulsion of the excess of sulphuretted hydrogen, mixed with a solution of tribasic acetate of

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lead; this caused a white precipitate, which, after being washed with water, dried at 212°, and analysed, furnished—

Carbon.....	9·77	56 =	4200·0	9·73
Hydrogen	1·04	33	412·5	0·95
Oxygen	11·87	51	5100·0	11·81
Oxide of lead	77·32	24	33468·0	77·51

Whence the authors deduce the formula $C^{56} H^{33} O^{51} + 24PbO$, $3(C^{18} H^5 O^{11}, 3PbO, HO) + 5(C^4 H^3 O^3, 3Pb)$.

A portion of the salts with which these various analyses were made was decomposed under water by a current of sulphuretted hydrogen. The liquid was separated from the sulphuret of lead, evaporated in the water-bath, and when sufficiently concentrated set aside in a shallow dish covered with paper. After a long time, perfect crystals of citric acid had formed. They were pulverized, dried *in vacuo* over sulphuric acid, and analysed. They gave—

Carbon.....	37·51	37·27	12 =	900·0	37·50
Hydrogen.....	4·45	4·41	8	100·0	4·16
Oxygen.....	58·04	58·32	14	1400·0	58·34

According to these experiments, *Richardsonia scabra* contains a considerable amount of citric acid in all its parts, and agrees in this respect with the *Stellatæ*, *Rubia tinctorum*, *Asperula odorata*, &c.

The property of acetate of lead of forming double compounds with other lead salts is well known; we are acquainted with similar combinations of acetate of lead with benzoate, kinovate of lead, &c. Heldt mentions, in his paper on citric acid, that, on dissolving tribasic acetate of lead in nitric acid and cooling, bibasic citrate crystallizes out, but that it always contains a certain amount of nitrate which cannot be removed by washing. Hence there likewise exists a compound of citrate with nitrate of lead.

To check their results, the authors dissolved pure commercial citric acid in water, and precipitated with solution of acetate of lead. The washed precipitate was dried at 212°, and analysed. The following are the results:—

Carbon.....	14·71	72 =	5400·0	14·90
Hydrogen	1·50	42	525·0	1·45
Oxygen	18·11	66	6600·0	18·22
Oxide of lead	65·68	17	23706·5	65·43

In this salt the presence of a certain amount of acetic acid was proved by analysis. The herb of *Richardsonia* appears to contain some aconitic acid besides the citric acid.—*Bericht der Wiener Academie.*

On the Action of Ammonia on Sebacic Æther.
By Thos. H. Rowney, F.C.S.

The following experiments were made to endeavour to ascertain, if possible, whether sebacic acid is a bibasic acid or not. I formerly intended to pursue the subject further, and to investigate the dif-

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ferent compounds and products of decomposition; but I am induced to publish my results now, in consequence of having seen in the 'Chemical Gazette' of October 1, 1851, a notice of a paper by M. Bouis, taken from the 'Comptes Rendus' of August 11, 1851, from which it appears that M. Bouis has been working in a somewhat similar direction. I had heard some time since from Dr. Hofmann that sebacic acid had been obtained from castor oil; and being then engaged in the examination of the action of ammonia on various oils, I intended to examine its action on castor oil, in order to compare the results obtained in this action with those obtained by acting with ammonia on the æthyle compounds of sebacic acid. I was not aware at the time that M. Bouis had examined this action; but as he has done so, and published some account of his results, I have not waited to complete my own experiments, but lay before the Society the results I have obtained by acting on sebacic æther with strong ammonia.

The æther employed for these experiments was obtained by passing a current of dry hydrochloric acid gas into an alcoholic solution of sebacic acid, and then adding water; when the æther had risen to the surface, the acid liquid was syphoned off, and the æther was washed with cold water. Thus obtained, it is an oily liquid of a fragrant odour, insoluble in cold water and very soluble in alcohol. The quantity obtained was too small to allow me to purify it by distillation, in order to ascertain its boiling-point.

In order to submit it to the action of ammonia, it was dissolved in alcohol, and digested in a stoppered bottle with a strong solution of ammonia. After digesting for about a month, a perceptible change took place in the æther; instead of an oily liquid, a bulky and somewhat granular substance made its appearance, from which bubbles of gas were given off. After continued digestion, the evolution of gas ceases, and the substance becomes more granular; and as all action had ceased, it was filtered, and washed with cold water until it was free from ammonia. To obtain it quite pure, it was twice crystallized from alcohol; it then exhibited the following properties:—

It is insoluble in cold water, rather soluble in boiling water, slightly soluble in cold alcohol, very soluble in boiling alcohol, and is deposited from this solution in hard, rounded, granular crystals; under the microscope, these are found to be collections of minute needle-shaped crystals. Its solutions are neutral to test-paper; it is insoluble in a dilute solution of ammonia; when boiled with a solution of caustic potash, it gives off ammoniacal fumes, but cold potash does not act upon it.

The following results were obtained by the analysis of the substance crystallized from alcohol, and dried at 100° C.; the combustions were made with oxide of copper and copper turnings:—

Carbon	59·86	59·95	60·02	20	=120	60·00
Hydrogen	9·94	9·78	10·32	20	20	10·00
Nitrogen.....	13·85	..	..	2	28	14·00
Oxygen	..	..	..	4	32	16·00

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These analyses show that the substance was the neutral amide, as will be seen on comparing the numbers obtained by analysis with those calculated.

The ammoniacal mother-liquor and washings were evaporated on a water-bath to a small bulk, and hydrochloric acid was added to it; a copious precipitate was obtained, which was filtered and washed with cold water. It was then dissolved in a dilute solution of ammonia, and filtered to separate it from a small quantity of the sebamide, reprecipitated by hydrochloric acid, filtered and washed until quite free from hydrochloric acid, and then crystallized from water. It is deposited from its aqueous solution in rounded grains, very similar in appearance to sebamide. It is very soluble in alcohol, and also in boiling water; its solution has an acid reaction. Analysis gave the following results:—

Carbon.....	59·61	59·68	20 =	120	59·70
Hydrogen	9·48	9·59	19	19	9·45
Nitrogen	6·70	..	1	14	6·96
Oxygen	..	..	6	48	23·89

These numbers agree closely with those calculated for the acid amide.

Sebamic acid when dry is very similar in appearance to sebamide, but differs from it in being very soluble in a dilute solution of ammonia; it gives off ammoniacal fumes when boiled with caustic potash. Its ammoniacal solution gives a precipitate with nitrate of silver, soluble in nitric acid and in excess of ammonia; it also gives a precipitate with acetate of lead, but does not precipitate the alkaline earths. Having but little of this substance, I have not been able to examine any of its salts.

From the results of these analyses, I conclude that sebacic acid ought to be considered as a bibasic acid, its formula being $C^{20} H^{16} O^6 . 2HO$, and that the æther obtained in the manner I have described is in reality a mixture of the acid and neutral æthers. If this be the case, the action of ammonia upon them may be readily explained. In the formation of the neutral amide we have—

$$C^{20} H^{16} O^6 . 2C^4 H^5 O + 2NH^3 = C^{20} H^{20} O^4 N^2 + 2C^4 H^5 O, HO,$$

and in the acid amide we have—

$$C^{20} H^{16} O^6 . \begin{matrix} C^4 H^5 O \\ HO \end{matrix} + NH^3 = C^{20} H^{18} O^5 N . HO + C^4 H^5 O, HO,$$

leaving in the acid 1 atom of hydrogen capable of being replaced by bases.

This action of ammonia I found to be constant, as in three separate preparations sebamide and sebamic acid were always formed.—*Quart. Journ. of Chem. Soc.*, Jan. 1, 1852.

Examination of the Seed and Capsules of Digitalis purpurea. *By* Dr. A. Buchner, sen.

The author has examined the seed and capsules of *Digitalis purpurea*. The seed lost by drying at about 162° F., 9·26 per cent. of

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water. The capsules are very slightly hygroscopic, and lose scarcely 4 per cent. by drying. The author prepared extracts of the seed and of the capsules with æther and water, and examined them. The following are the results arrived at:—

The seeds of *Digitalis purpurea* are preferable to the leaves, as they contain a larger amount of digitaline together with a fat oil, are not so liable to be mistaken or collected at a wrong period, and are more easily dried and preserved without experiencing any alteration; in short, more dependence can be placed upon them.

The digitaline in the oily compound, which is easily prepared with æther from the seed, merits every attention in a therapeutical respect, for the seed, or the oily digitaline compound from it, can be easily dispensed, and at a very moderate expense, in various forms, as emulsion, powder, pills, &c.

The seed-capsules and calyx of *Digitalis* likewise contain digitaline, but in proportionately far smaller quantity; so that the tannate of digitaline, which can be prepared from the aqueous extracts, is respectively as 3·00 and 0·33 per cent. of the weight of the seed and capsules.

This quantity, separated from the seed by exhaustion with boiling water, does not form the entire amount of digitaline; for, like resinous substances, it is not only soluble in alcohol, but also in oils, and it is partially combined with the fat oil of the seed.

The oil containing the digitaline, which can be extracted by æther, amounts to about 40 per cent. of the weight of the seed; it belongs to the siccative oils. Æther extracts, besides the oil, another more resinous digitaline compound, which sinks in water, while the oil floats on the top. A portion of the digitaline compound can be removed from the oil by water.

The tannate of digitaline is soluble in hot water; on cooling, it again separates for the greater part.

Digitaline prevents the fermentation of an aqueous solution of sugar; it must therefore be considered as a poison to beer-yeast.—Buchner's *Repert.*, ix. p. 38.

On the Production of Saltpetre and Soda in Hungary. *By* Jos. Szabó *of Pesth.*

Professor Szabó describes the methods employed in Hungary to procure saltpetre, from which it receives the following technical names:—

Gay Saltpetre.—This is the kind obtained by washing the earth dug from the floors of the rooms occupied by the poorer classes, to whom boarded floors are unknown. The nitre-boilers prefer the gay earth to all other materials. Although it affords only a poor lye of 2°–3°, it yields a purer saltpetre, with no other impurity than chloride of sodium. Therefore even the government regulations against the manufacture of nitre from this source have met with no success.

Plantation Saltpetre is now obtained almost exclusively from those plantations belonging to Baron v. Vay, near Debreczin, established at the time of the war with France, and which are still

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regularly worked. They consist of nearly 1000 pyramids, 12 feet in length, 3–4 feet broad, and 6–8 feet high, composed of two-thirds washed gay earth and one-third ashes. As they are entirely uncovered, they do not yield more than about 300 cwt. of saltpetre annually, while rather more than 50 gay-earth heaps at Bicske are said to yield more than 200 cwt. annually. These pyramids are scraped down three or four times a year, and the part removed washed with water to extract the salt.

Kehr Saltpetre is produced at the kehr places (*Salétromszérü*), which occur most frequently near Debreczin, in the district between the Theiss and Marosch. There are also saltpetre kehr places at the military boundaries near Alibunár. The boiling-house at Debreczin is said to have been established more than two hundred years. In Debreczin itself there is an artificial and not very productive kehr place near the boiling-house, as well as also a few plantations, and besides these the natural kehr places of twenty-four villages belong to the town. These far more productive natural kehr places are always situated in the immediate neighbourhood of the villages; the most important are at Mike-Pércs, Paláyi, Vértes, Ascád, Sz. Mihály, Nánás and Szoboszló. The workmen are all inhabitants of the villages, and carry on the manufacture of saltpetre in conjunction with agriculture. Szabó visited one of the principal kehr places, that at Mike-Pércs, during the most favourable season, and ascertained all the particulars connected with it, which he states to be essentially the same at all the others.

The kehr place at Mike-Pércs is situated upon a gently sloping ground between the village and a marsh, which is never quite dry. It does not, like the natural soda kehr places in Hungary, yield the salt directly; but it is necessary that the earth, consisting of loose black sand mixed with chalk and clay, which formerly was a part of the marsh, should be strewed from time to time with ashes, especially straw-ashes, in order to make the salt come out upon the surface. The constantly moist ground receives the organic matters, partly from the marsh and partly from the village, all the drainage from which flows to the marsh. As manure is not used there to put upon the land, but only for making banks round the fields, the saltpetre grounds receive a sufficient supply of appropriate material. Under these favourable circumstances, the saltpetre is formed, chiefly in May and June, even during twenty-four hours, in such quantity that it can be collected every evening. The uppermost surface of earth is scraped off by means of an iron, shaped like a knife, which is dragged by a horse, and the saline earth swept together and collected, while all the irregularities of the ground are again carefully leveled.

The establishment of a new kehr place is preceded by a formal examination, in which attention is paid to the occurrence of certain narcotic plants. Upon such ground as is suitable for kehr places, very good tobacco grows, which however is not used in consequence of its deflagrating in the pipe. All plants which assimilate saltpetre are carefully removed from the kehr places.

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With regard to the geognostic relations of the kehr places, Szabó remarks that the efflorescent product of the kehr places contains not only potash saltpetre, but other salts as well, such as sulphate of magnesia, and especially carbonate of soda, sometimes in such quantity, that it is preferred to make use of the kehr saltpetre in the soap factory at Debreczin.

The formation of kehr saltpetre stands in evident connexion with that of kehr soda. Besides the saltpetre and soda district of Debreczin, the soda region forms a broad band running through the centre of the great Hungarian plain, especially of the sandy ground in the Pesth and Bács districts. There are in this direction a great number of lakes and marshes, the waters of which are not in all cases saline. In the saline lakes, the greater part of the soda effloresces, not immediately at the water's edge, but upon that part of their banks which is left dry by the evaporation in warm weather. This spot becomes covered with an abundant coating of soda, which is collected by sweeping it together. However, soda kehr places sometimes occur in situations which are considerably more elevated than those lakes. Szabó refers the formation of soda to the action of carbonate of lime in solution upon silicates of soda. He is of opinion that carbonate of potash is formed in a similar manner, but that on account of its ready solubility it remains unobserved.

The detailed description of the processes of washing the kehr earth, and the refraction of the lye, that is the addition to it of an alkaline lye, the extraction of raw saltpetre by evaporation, and the refining of the saltpetre, which operations are for the most part carried on by the country people themselves, testifies to the already advanced state of the manufacture of saltpetre in Hungary, which it is probable however may still admit of considerable extension.—*Archiv der Pharm.*, vol. lxvi. pp. 311–316.

On the Changes which Tartaric and Racemic Acids experience at a high Temperature. By E. Fremy.

Laurent and Gerhardt have submitted Fremy's former researches on tartaric and racemic acids to criticism, and have endeavoured to show that both these acids likewise form no exception to the law which is generally applicable to acids according to these chemists. According to their view, the acids are analogous to a salt; the anhydrous acids (anhydrides) are incapable of combining with bases.

Fremy, on the contrary, considers the anhydrous acids, with the majority of chemists, as true acids. The phænomena of saturation, which in Laurent and Gerhardt's view lose all importance, constitute with Fremy the fundamental difference between acid and salt, so that the sulphates and the hydrate of sulphuric acid cannot be arranged in one group of bodies.

In refutation of the doubts raised by Laurent and Gerhardt against the views he had brought forward with respect to tartaric and racemic acids, according to which the changes which these acids experience by heat are dependent on the elimination of water,

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Fremy has again taken up his investigations on these two acids, and has proposed to himself first of all to answer the question, whether the modifications which tartaric acid and racemic acid undergo on being heated to 338° F. result, according to Laurent and Gerhardt's assertion, from a mere transition into an isomeric state, or from the gradual escape of the hydrate-water of these acids; and whether generally the influence of the water on the saturating capacity of the inorganic acids does not equally apply to the organic acids.

Assuming with Laurent and Gerhardt that the modifications of racemic and tartaric acids are not owing to a loss of water, but to a transition into an isomeric state, then Graham's views respecting the modifications of phosphoric acid have no value, and we must again admit the earlier opinions concerning the isomerism of phosphoric and pyrophosphoric acids.

Fremy further expressly observes, that the discoveries made of late years are in favour of Graham's views, which are adopted by most chemists; he admits the importance of the influence of the amount of water in relation to the properties of the acids and their saturating capacities, and these views may be satisfactorily applied to the substances which are produced in the distillation of tartaric and racemic acids.

According to Fremy's former investigation, tartaric acid parts with water at 338°, and is converted into three acids. The first, tartralic acid, is sesquibasic; its formula is $C^8 H^4 O^{10}, 1\frac{1}{2}HO$; it combines with $1\frac{1}{2}$ equiv. base to a neutral salt, is not crystallizable, and forms with lime a salt which is readily soluble in water. The second, the tartrelic acid, is monobasic; its formula is $C^8 H^4 O^{10}$, HO; it combines with 1 equiv. base to a neutral salt, is uncrystallizable, and forms with lime a tenacious salt, which is perfectly insoluble in water. The third is anhydrous tartaric acid, $C^8 H^4 O^{10}$; it is insoluble in water, but gradually recombines with it, and, passing through the intermediate states of tartrelic and tartralic acids, is finally reconverted into ordinary tartaric acid, $C^8 H^4 O^{10}$, 2HO.

Now exactly the same occurs with racemic acid. Fremy considers the investigation of Laurent and Gerhardt as confirming his views. The substance which these chemists have called isotartaric acid is Fremy's tartralic acid, the isotartridic acid is Fremy's tartrelic acid. Laurent and Gerhardt have also confirmed the existence of the anhydrous tartaric acid. But with respect to the constitution of these acids, Laurent and Gerhardt consider tartralic acid as isomeric with tartaric acid; the latter consequently must be converted into tartralic acid without any loss of water. According to them, tartralic acid is monobasic; its salts are MO, $C^8 H^4 O^{10}$. They view tartrelic or isotartridic acid as isomeric with anhydrous tartaric acid, $C^8 H^4 O^{10}$; its salts are MO, $C^8 H^3 O^9$. The formula proposed by Laurent and Gerhardt for the tartrelates consequently contains 1 equiv. less water than Fremy's.

In opposition to this, Fremy finds the view he formerly expressed confirmed by his recent investigation. Tartaric and racemic acids are converted, at an elevated temperature, before yielding empy-

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rematic products, into the three acids, which are distinguished by their different amount of hydrate-water and their saturating capacity. With the exception of the metatartaric acid of Laurent and Gerhardt, all the acids described by those chemists had already been described by Fremy.

1. Tartralic acid is, according to Fremy, not merely isomeric with tartaric acid, as he finds that its formation from tartaric acid at 338° is constantly accompanied by a loss of water, and that the quantity of tartralic acid produced is always proportional to this amount of water. Fremy prepared the tartralate of lime by melting the tartaric acid at 338°. The melting was interrupted at the three most different periods of the reaction, viz. 1st, at the commencement of the formation of tartralic acid; 2nd, when the whole of the tartaric acid had passed into tartralic acid; and 3rd, when tartrelic acid began to form. It was then neutralized with chalk, the tartralate of lime precipitated by alcohol, dried first *in vacuo*, and then at 248°. Fremy concludes, from the constant results of the analyses of the tartralates, that the salts prepared in this manner are obtained pure, and contain but a mere trace, if any, of metatartaric acid, which Laurent and Gerhardt supposed to be mixed with this salt.

The lime salt corresponding to the formula $CaO^{1\frac{1}{2}}, C^8 H^4 O^{10}$, which requires 24·1 per cent. of lime, furnished 23·8 and 23·6 per cent. The lead salt corresponding to the formula $(PbO)^{1\frac{1}{2}}, C^8 H^4 O^{10}$, which requires 55·9 per cent. of oxide of lead, furnished 55·9 per cent. of oxide of lead.

Laurent and Gerhardt prepared the tartralate of lime according to a different process, which Fremy considers to be erroneous. Tartrelate of ammonia was converted by the action of an excess of ammonia into tartralate, and then acetate of lime and alcohol added to the liquid, when a tenacious mass separated, which was repeatedly washed with alcohol. Laurent and Gerhardt considered this mass as pure tartralate of lime. Fremy concludes, from its mode of preparation, that it contains some of all the other matters formed in the process from its being obtained as a tenacious mass, and it consequently might readily contain too little lime.

2. With respect to tartrelic acid, Laurent and Gerhardt suggested that 1 equiv. water should be deducted from the general formula of these salts. Fremy, on the contrary, asserts that this question cannot be decided by the determination of the capacity of saturation; whilst the elementary analyses of the tartrelates confirm the formula given in his former memoir. Moreover, the assumption on the part of these chemists, that this acid contains less water than tartaric acid, is in favour of Fremy's view. Their assertion, that the amount of base found in a tartrelate agrees better with the formula $MO, C^8 H^3 O^9$ than with the formula admitted by Fremy, $MO, C^8 H^4 O^{10}$, is refuted by the following analyses:—

Tartrelate of lime furnished in repeated analyses 17·4 and 17·0 per cent. of lime. Fremy obtained by elementary analysis the following

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results:—I. is tartrelate of lime dried *in vacuo*; II. dried at 248°; III. dried at 248°; IV. at 286°:—

	I.	II.	III.	IV.		
Carbon.....	27·7	30·3	30·6	30·8	8	30·0
Hydrogen	3·5	2·3	2·5	..	4	2·5
Oxygen	53·1	50·4	49·4	..	10	50·0
Lime	15·7	17·0	17·5	16·9	1	17·5

3. Anhydrous tartaric acid is by no means isomeric with tartrelic acid. Fremy could never succeed in converting the tartrelic acid into anhydrous tartaric acid without the former first having lost the 1 equiv. water, by which amount the two acids differ from each other. At 338°, the temperature at which the metamorphosis occurs, not only water escapes, but likewise acid vapours of carbonic acid and empyreumatic acids.—*Ann. der Chim. et de Phys.*, xxi. p. 329.

ANALYTICAL CHEMISTRY.

On the Estimation of Bromine. By L. Figuier.

The estimation of bromine, that is to say, the determination of the amount of this body in a mixture of chlorides and bromides, is one of the most difficult operations in chemical analysis. "Chlorine and bromine, and the corresponding chlorides and bromides," says Prof. H. Rose in his 'Analytical Chemistry,' "have so much analogy, that we are as yet unacquainted with any accurate method of separating bromine from chlorine."

It is not my intention to pass in review the different processes which have been suggested or employed for the estimation of bromine. Every chemist is aware that they are all accompanied by difficulties even when the amount of bromide is considerable, and that their application is impossible, or exceedingly erroneous, when the bromides are in small proportion relative to the chlorides: such, however, is most generally the case; as in the mineral waters, those of the ocean and of the salt lakes, the mother-liquors of the salt-works, &c., in which the bromides are frequently associated in small proportion with considerable quantities of chloride of sodium and other chlorides. In this case the employment of the processes described in treatises on analytical chemistry is perfectly deceptive. Having frequently had occasion to verify this fact, I endeavoured to find a process which would allow the amount of bromine to be readily determined in mixtures, even when present in minute quantity; and I think I have solved the problem by means of a *standard solution of chlorine*. Several difficulties however presented themselves: in the first place, how was it possible, there being no formation of precipitate, to ascertain the precise moment when the bromide ceases to be decomposed by the chlorine? The following

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observation however enabled me to overcome this difficulty. If we take a saturated aqueous solution of bromine, and consequently having a deep yellow colour, and boil it for a few minutes, the bromine gradually disappears entirely, and the liquid soon becomes perfectly colourless. This fact evidently enables us to analyse the bromides by a solution of chlorine; the bromide being decomposed by chlorine, the liquor assumes a deep yellow colour from the liberated bromine; but by boiling the liquid, the bromine is expelled, and the liquid left perfectly colourless, so that a fresh addition of chlorine can be made, and the treatment repeated until complete cessation of reaction, which is readily ascertained from a further addition of chlorine no longer imparting a yellow colour to the liquor.

It was necessary, before putting this process into practice, to obtain information on sundry points. In the first place, it was requisite to ascertain to what extent a normal solution of chlorine might be employed in accurate analysis. It is generally considered that a solution of chlorine in water is rapidly decomposed; experiment proved that by taking the precaution to keep the solution of chlorine in a bottle covered with black paper, in order to protect it from the light, the decomposition of the water is so slow as to be of no importance, and does not interfere with the permanence of the strength of the solution. I took a solution containing 0·5 grm. of bromide of sodium; it required 115 divisions of chlorine to be entirely decomposed. The experiment was repeated after an interval of twenty-four hours with the same quantity of salt and the same solution of chlorine; it required 122 divisions to produce the same effect. The decomposition was somewhat more active with weaker chlorine-water. A solution containing 0·5 grm. of bromide of sodium required for its complete decomposition 260 divisions of chlorine-water. On repeating the experiment twenty-four hours later, 295 divisions were necessary to obtain the same effect. These results show that the decomposition of the solution is so slow as not to interfere with its employment as a standard solution. Taking care to determine the strength of the liquid just before using it, the interval of about half an hour required for the analysis can have no influence on the result. When I had occasion to make the analysis of several mixtures at the same time, an operation which required several hours, I determined the strength of the chlorine solution at the beginning and at the end of the experiments, and took the mean of the two numbers. The difference between these results, obtained at an interval of some hours, was so small that it could be neglected; converted into weight of bromide, it did not represent more than some tenths of a milligramme, a quantity not appreciable by the balance.

Theory indicates that any soluble bromide may be employed to determine the strength of the solution of chlorine. Thus a solution of chlorine, the strength of which has been ascertained by means of bromide of sodium, can be used to determine not merely the quantity of bromide of sodium present in a liquid, but also the bromide

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of potassium, magnesium, &c.; for according to the law of equivalents it is always the same weight, or 1 equiv. of bromine, which is combined with the several metals, and the quantity of chlorine requisite to expel the bromine from its combination is always the same with whatever metal it is combined. Although the truth of this result might be established *à priori* by theory, it was requisite to establish its reality by experiment.

I therefore dissolved 0·5 grm. of bromide of sodium in water, and decomposed the solution accurately with a normal solution of chlorine; 244 divisions were required. On the other hand, I dissolved 0·5 grm. of bromide of potassium in water, and found, by employing the same normal solution, that 212 divisions were necessary. This result agrees with theory. 0·5 grm. of bromide of sodium contain, according to the known composition of this salt, 388 milligrms. of bromine, and 0·5 bromide of potassium contain 335. 244 divisions of the chlorine solution were necessary to expel from its combination the 388 milligrms. of bromine in the bromide of sodium. We have therefore—

$$0{\cdot}388 : 244 :: 0{\cdot}335 : x = 210,$$

a number which comes sufficiently near to 212, the one obtained by experiment. A solution, the strength of which has been determined by means of bromide of sodium, can consequently be used for ascertaining the amount of bromine in the state of bromide of potassium, magnesium, &c. It gives the absolute quantity of bromine, which can then be referred to the different metals to which it is united.

The mother-liquors of the salt-works in which bromine occurs have frequently an alkaline reaction, at times resulting from the operations of analysis; as, for instance, when sea-water and mineral waters containing chlorides or bromides of magnesium are evaporated to dryness, the chloride of magnesium is decomposed by heat, which sets free some hydrochloric acid, and leaves a basic subsalt in the liquid.

This would cause an error in the use of normal solutions of chlorine, for the small quantity of magnesia or magnesian subsalt would absorb a certain amount of chlorine, which would be falsely attributed to decomposed bromide. To avoid this error, the liquid must be acidified. I found that if hydrochloric acid is used for this purpose, the result is in no ways influenced by it. I decomposed with a standard solution of chlorine 0·3 grm. of perfectly neutral bromide of sodium; it required 118 divisions. I repeated the same experiment after having added to the liquid 10 drops of hydrochloric acid. The operation furnished the same result as with the neutral solution; in both cases exactly the same number of divisions was employed. The presence of hydrochloric acid, therefore, does not alter the result.

The following facts will show the degree of precision to which it is possible to attain by this method. If we dissolve in water 5 milligrms. of fused bromide of potassium, the liquid is coloured strongly yellow by the action of weak chlorine; the colour disappears by

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boiling, but a fresh addition of chlorine colours it anew. When the water, instead of being pure, is charged with salts, 5 milligrms. of bromide of potassium are not readily detected by chlorine-water, but 1 centigrm. of bromide is easily discovered. I dissolved in distilled water 45 grms. of pure common salt, and added to the liquid 1 centigrm. of fused bromide of potassium. With chlorine-water the liquid turned yellow; this disappeared on ebullition, but was again called forth by more chlorine. 1 centigrm. of bromide of potassium in a saline solution will consequently be ascertained without difficulty, and even its quantity determined by this method.

The following is the mode of operating:—A solution of bromide of sodium is prepared, containing a known weight of the salt in a determined volume of distilled water; I generally use a solution of 2 grms. of bromide of sodium in 400 cub. centigrms. of water; 100 cub. centims. of this solution therefore contain 0·5 grm. of bromide of sodium. This liquid serves to determine the strength of the solution of chlorine just before the analysis. For this purpose we add to 100 cub. centims. of the solution a few drops of hydrochloric acid; we then ascertain what volume must be used to effect the decomposition. A graduated tube, divided into 100 equal parts, serves to contain the solution of chlorine. [The small burette divided into 100 parts is highly advantageous, and may be stopped with a cork, so as to avoid loss of chlorine.] In the course of the operation, it is advisable to keep it surrounded by black paper, which is only removed in order to read off the divisions.

This graduated eprouvette being simply filled with chlorine-water, a certain quantity of the reagent is added to the normal solution of bromide of sodium contained in a small glass flask; the liquid is coloured strongly yellow by the liberated bromine; it is then boiled for a few minutes, when it becomes perfectly colourless; it is removed from the fire, and let cool for one or two minutes, and then more chlorine added; the liquid is again boiled, the bromine is expelled, and the liquid becomes colourless. By repeating this operation, we are able to determine in an approximative manner the number of divisions of chlorine required to decompose the normal solution. This term being known, the same operation is repeated a second time, which enables us to determine definitively the strength of a normal solution.

We now proceed to the determination of the bromine contained in the liquid under examination. For this purpose the same method is pursued as for determining the strength of the chlorine liquid; for instance, if it is a mineral water, it is previously concentrated in a flask, acidulated with 8 or 10 drops of hydrochloric acid, and the amount of chlorine required for the liquid no longer to exhibit any trace of yellow colouring ascertained by the preceding method. The strength is approximatively determined by a first operation, and definitively by a second, in which the same quantity of mineral water is used. The number of divisions of chlorine requisite to decompose the whole of the bromide in the mineral water being known, we have all the elements of the analysis; in fact, it suffices to esta-

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blish a proportion, to ascertain how much bromide of sodium the quantity of chlorine consumed represents, and then to calculate the quantity of bromine by weight which the bromide of sodium represents.

Besides being accurate and easily executed, this method has a great superiority over the old ones, inasmuch as it admits at the same time of ascertaining the state in which the bromine exists in a mineral water.

When a solution of bromide of magnesium in water is evaporated to dryness, towards the end of the operation the salt is partially decomposed, and there is a very perceptible disengagement of hydrobromic acid. We can take advantage of this fact to determine whether the bromine in a mineral water is combined with sodium only or united with magnesium. Two operations are requisite. In the first, the total amount of the bromine present is determined by the normal solution of chlorine; the same quantity of mineral water is then evaporated to dryness. To facilitate as much as possible the total decomposition of the bromide of magnesium, a little water is added to the dry residue, and the whole again evaporated to dryness. By repeating this six or seven times, it may be taken for granted that the whole of the bromide of magnesium has been destroyed and lost its hydrobromic acid. If therefore we redissolve this residue in water, add a few drops of hydrochloric acid, and determine the quantity of bromine which it now contains, we find, if any bromide of magnesium existed in the mixture, a lower number than before. The difference between the two numbers evidently represents the bromine which has disappeared during the evaporation, and which belonged to the bromide of magnesium. If, on the contrary, the result of the two operations gave no difference, we are justified in concluding that the whole of the bromine present was in the state of bromide of sodium.

The following are examples of the two cases. I took 58·85 grms. of the mother-water of the Kreutznach salt-works, of the specific gravity 1·293, and determined, without evaporating it, the quantity of chlorine required to expel the whole of the bromine which it contained; 270 divisions of chlorine were consumed. I then took 55 grammes of the same mother-water, evaporated it to dryness, and added distilled water to the residue five or six times. On dissolving the residue in water, adding a few drops of hydrochloric acid, I found that only 208 divisions were required to expel the bromine existing in the residue. Calculating upon these data, I find that the Kreutznach brine contains in 1 kilogrm. of liquid 8·7 grms. of bromide of sodium and 2·6 grms. of bromide of magnesium. Operating in the same manner, I found that 1 kilogrm. of the brine of Nauheim contains 2·60 grms. of bromide of sodium and 1·43 of bromide of magnesium, and that the brine of Salis in Béarnais, of the specific gravity of 1·218, contains 1·60 of bromide of sodium and 63 centigrms. of bromide of magnesium.

In the following analysis of the water of the Mediterranean I was able, by means of this method, to prove that the whole of the bro-

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mine is contained in the state of bromide of sodium. I took 1 litre of the water collected at Cette at some distance from the coast, and concentrated the liquid until it occupied a volume of 112 cub. centims., M. Uziglio, in his analysis of the water of the Mediterranean, having shown that the bromide of sodium begins to separate when the water indicates 25° on the areometer. I then determined, by a normal solution of chlorine, the amount of bromide of sodium, and found that it contained 121 milligrms. in the litre. I then took 1 litre of the same water, evaporated it to dryness, redissolved and re-evaporated it five times in order to decompose the earthy bromides, if any existed in the residue. The saline mixture was redissolved in water, filtered, mixed with a little hydrochloric acid, and analysed with the normal solution. I now found 119 milligrms. of bromide; the difference between these two numbers is so small, that they may be regarded as identical; whence it would result that 1 litre of the water of the Mediterranean taken at Cette contains 121 milligrms. of bromide of sodium and no bromide of magnesium. This number differs considerably from that published by M. Uziglio, who found 570 milligrms. of the same salt in 1 litre of water collected in the same locality.

The examples above cited will suffice to show how the process may be employed to ascertain in what state the bromine is contained in mineral waters, in which hitherto the only compounds of bromine met with are the bromides of sodium and magnesium.

I have now to notice some difficulties which might occur in the carrying out of this process, and to point out the means of avoiding them. Perceptible errors might occur in the case of mineral waters containing a salt of iron or manganese; the chlorine would be absorbed by the oxides, converting them into peroxides; it is therefore necessary, before proceeding to the determination of the bromine, to separate the whole of the oxide of iron or manganese. As the oxide of iron is precipitated by boiling, it suffices to evaporate the liquid nearly to dryness to avoid this source of error.

The amount of bromine has frequently to be determined in the mother-liquors of salt-works. It sometimes happens, when these waters have long been exposed to the air, they acquire a deep yellow colour, which might be confounded with that of the bromine; and, moreover, this colour is sometimes owing to organic substances, which might combine with a little of the chlorine, and so cause an error in the result; it is therefore requisite to destroy this colouring. Charcoal was not found to answer, but the addition of a few drops of bromine, and subsequent ebullition to expel the excess, succeeded completely. I ascertained by experiment, that, provided the liquid was kept acid, it retained no trace of bromine; and that in this case this substance might be used without any fear of causing an error in the analysis.

The presence of a considerable quantity of organic matter in the mineral waters would complicate this new method; however, organic substances are rarely found to any amount except in sulphurous waters. A difficulty would also occur in the case of the liquid con-

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taining iodides. In this case the chlorine would be consumed to expel the iodine, and a very serious error would be committed by referring this quantity of chlorine to the account of the bromine. To avoid this error, the iodine is separated by chloride of palladium, the excess of palladium by sulphuretted hydrogen, after which the liquid is boiled for some time to dissipate completely every trace of sulphuretted hydrogen, which would otherwise act upon the chlorine. The presence of iodine, together with bromine and chlorine, in mineral waters, is however very rare. In the numerous analyses of bromine-waters, which I made in conjunction with M. Mialhe, I never met with iodine together with bromine either in mineral waters or in the mother-waters of the salt-works. I have several times had occasion to examine sea-water for iodine; and although the existence of iodine in marine plants points to its presence in the water, I have never succeeded in demonstrating it. The existence of iodine in the water of Balaruc had recently been announced, but I could not detect it in the residue from 10 litres of water.

The employment of a normal solution of chlorine is not the only method which can be used to determine with accuracy the amount of bromine in combinations or mixtures. I have used successfully another method, based upon wholly different principles, and which I think equally susceptible of great accuracy. It requires more time than the preceding; it may however prove useful, and may be applied with advantage to check the results furnished by the preceding method. It consists essentially in the use of chlorine and æther to remove the bromine, and the conversion of the bromine thus isolated into bromide of sodium, which is then decomposed by chlorine. The difference between the weight of the chloride and bromide of sodium united, and the weight of the remaining chloride, after decomposition of the bromide by chlorine, indicates the quantity of bromine sought.

Serrulas proposed a process founded upon analogous principles; but its execution was so faulty, that no dependence could be placed upon the results it furnished. The following is the second method:— The concentrated mineral water, or the solution containing the bromide, is placed in a ground stoppered bottle, its volume of æther added, then the chlorine solution, and the mixture well shaken. After some time the bromine dissolved in the æther floats on the surface. To ascertain whether the quantity of chlorine is sufficient, a little of the solution of chlorine is conveyed into the aqueous portion of the liquid by means of a pipette with a long stem. When the quantity of chlorine added is sufficient, it is known from the liquor turning yellow by the liberated bromine at the spot where it is in contact with the chlorine; or a little of the aqueous solution is removed with the pipette and tested with chlorine. When the addition of 1 drop of chlorine renders the liquid perfectly colourless, it is a sign that the whole of the bromide is decomposed. When this is the case, the ætherial liquid containing the bromine is removed with the pipette, and a little fresh æther added to take up the last trace of bromine, which is then also removed with the pipette.

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In this manner it is possible, by acting with precaution, to separate the whole of the bromine without removing any of the saline liquid.

The æther containing the bromine is conveyed into a medicine-phial containing some solution of soda in alcohol; it is entirely decolorized by the alkaline liquid, and is converted into bromate and bromide. The æther floats on the surface entirely decolorized. The contents of the phial are emptied into a porcelain dish, and placed on a sand-bath, which is gradually heated to expel the æther. Sometimes a minute quantity of a resinous substance, due to the action of the potash upon the æther, separates; it is removed by filtration, and the liquid now accurately saturated with hydrochloric acid, so as to convert the soda into chloride. The whole is then evaporated to dryness, when it furnishes a mixture of chloride and bromide of sodium with a little bromate of soda. In order to decompose this bromate, it is calcined, at a dark red heat, in a covered platinum crucible, until it becomes somewhat pasty, but does not fuse; otherwise a little chloride and bromide would be volatilized. In this calcination the salt turns slightly black. The calcined mixture is now carefully weighed and dissolved in distilled water, the carbonaceous residue collected upon a filter, and weighed when its weight is appreciable. Its weight is deducted from that of the mixture.

It now only remains to convert the bromide into chloride, in order to appreciate, by the difference of weight which this decomposition causes, the amount of bromine. For this purpose, the saline mixture, dissolved in water, is placed in a glass flask, acidulated with a little hydrochloric acid, and treated with an aqueous solution of chlorine; the liquid is immediately coloured yellow by the freed bromine. It is boiled to expel the bromine, and a little more chlorine added; if it still turns yellow, it is again boiled, and in this manner the whole of the bromine expelled, and its place taken by chlorine. This solution is now evaporated to dryness, the residue heated to redness in a covered platinum crucible, and weighed; the difference between the two weighings gives the weight of the bromine. In fact, the amount of bromine sought is to the difference of these two weighings as the atomic weight of bromine is to the difference of the atomic weights of bromine and chlorine. On multiplying this difference by 1·7947, that is to say by the equivalent of bromine divided by the difference of the equivalents of bromine and chlorine, we obtain a number which expresses the quantity of bromine existing in the mixture.

I proposed in this paper merely to take notice of the processes which might be employed for the estimation of bromine; considering however the close analogy between bromine and iodine, it will readily be conceived that the method of analysing the bromides by means of a normal solution of chlorine may be applied to the estimation of iodine. It suffices to take a solution of bromine, and fix its strength with a known quantity of soluble iodide; this solution may

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then be employed to appreciate the amount of iodide in a saline mixture.

This method, I am aware, loses much of its importance when applied to iodine, which can be accurately separated by sulphate of copper and chloride of palladium; but in those cases where a quick result is desired, the employment of a normal solution of bromine has many advantages, for instance in ascertaining the purity of the iodides of potassium of commerce, which at present are sadly adulterated. The process proposed by M. Berthet, in 1846, based upon the reaction of an alkaline iodate and sulphuric acid upon iodide of potassium, is not to be compared with the one which I propose.

M. Berthet forms a normal solution with iodate of soda and a small quantity of sulphuric acid, and appreciates the quantity of iodide by decomposing this salt with the normal solution. The whole of the iodine is eliminated:—

$$IO^5, NaO + 5IK + 6SO^3 = SO^3, NaO + 5SO^3, KO + 6I.$$

The liquid is boiled to expel the iodine, and in this manner the point ascertained when the iodine has altogether disappeared.

The solution of bromine is prepared by taking a saturated aqueous solution of bromine, obtained by leaving an excess in contact with distilled water for twenty-four hours, and diluting the solution with 12 times its volume of water; its colour is a pale yellow. The strength of this solution is determined by means of pure iodide of potassium.

When the normal solution of bromine is poured into a solution of an iodide, the liquid assumes a dark yellowish-brown colour, and when the liquid is heated, violet vapours of iodine are disengaged; the liquid soon becomes clear and perfectly colourless. It is somewhat more difficult to seize the precise moment when the decomposition is complete, owing to the somewhat yellowish colour of the bromine-water; but with a little practice this difficulty is soon overcome, and the process presents as much accuracy as in the estimation of bromine by means of chlorine.—*Ann. de Chim.*, Nov. 1851.

Detection of Manganese in Limestone Rocks.
By Prof. E. J. Chapman.

A considerable number of limestone rocks contain a minute proportion of carbonate of manganese. I have noticed this more particularly in the darker magnesian limestones of the Permian epoch, but also in various other limestones of different ages and from different localities. The common blowpipe-test—fusion with carbonate of soda—generally of so delicate an appreciation, here fails, even on the addition of nitre, to point out the presence of manganese. This is owing to the insolubility of the limestone in the carbonate of soda. If, however, a very small quantity of borax be added, so as to attack and dissolve a portion of the mass, the well-known greenish-blue enamel is quickly produced.—*Phil. Mag.* for February 1852.

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THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Examination of the Herb of Asperula odorata. *By* R. Schwarz.

The herbaceous part of *Asperula odorata* contains a fragrant substance, the identity of which with the stearoptene of the Tonka beans and the odoriferous constituent of *Trifolium melilotus* and *Anthoxanthum odoratum* was shown by Bleibtreu. The other constituents of this plant remained unknown. The author has now submitted it to closer examination.

He found in it, in addition to the coumarine, a peculiar tannic acid, which coloured persalts of iron of an intense green, and the same acid which Rochleder discovered in the root, and Willigk subsequently in the herbaceous part of madder, and which Rochleder has named rubichloric acid, characterized by the property of furnishing a green product of decomposition insoluble in water, when heated with hydrochloric or sulphuric acid. The tannic acid the author calls aspertannic acid. The aspertannic and rubichloric acids and the coumarine form the principal constituents of the green part of *Asperula odorata*; two other acids occur in it in small quantity, one of which appears to be catechuic acid, the other citric acid.

Aspertannic Acid, $C^{14}H^{9}O^{9}$.—The aqueous decoction of the herb of *Asperula odorata* is coloured dark green on the addition of a dilute solution of a persalt of iron. This reaction arises from the presence of aspertannic acid. A solution of acetate of lead produces a dirty green precipitate, which contains sulphuric, phosphoric, aspertannic, and probably catechuic acid, citric acid, partially-altered chlorophylle, small quantities of fat, and some coumarine. When the liquid filtered from this precipitate is mixed with tribasic acetate of lead, a beautiful lemon-coloured precipitate falls, which likewise contains aspertannic acid, some rubichloric acid and traces of coumarine.

The liquid filtered from this precipitate gives with ammonia a precipitate, which contains rubichloric acid and sugar.

In order to obtain compounds of aspertannic acid, the author endeavoured to prepare some lead salts, it being impossible to produce compounds with other bases. Potash, soda, lime and baryta, placed in contact with the acid, increase its tendency to absorb oxygen so much, that it is not possible to prepare a compound of any one of these bases with the unaltered acid; persalts of copper are converted into a compound of the oxidized acid with protoxide of copper.

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The lead salts employed for analysis were prepared in the following manner:—The herb of the *Asperula* was exhausted with boiling alcohol, the decoction filtered, the greater portion of the alcohol removed by distillation, the residue mixed with water, and filtered from the separated green flakes, consisting of chlorophylle and a little fat. The filtered liquid has a brownish-green colour, and gives with an aqueous solution of neutral acetate of lead a dirty green tenacious precipitate, which was washed with water and then treated with acetic acid. One portion remains undissolved in the moderately dilute acetic acid, whilst another portion dissolves with a yellow colour. The filtered solution was partially precipitated with absolute alcohol; the gray precipitate which first made its appearance was removed, and then absolute alcohol added as long as a precipitate resulted. This was collected upon a filter, washed with absolute alcohol, and dried at 212°. It was found to have the following composition:—

Carbon.....	25·85	56 =	336·00	25·79
Hydrogen	2·50	33	33·00	2·53
Oxygen	20·68	33	264·00	20·29
Oxide of lead	50·97	6	669·36	51·39

This leads to the formula $C^{56}H^{33}O^{33},6PbO=4(C^{14}H^{8}O^{8})+6PbO+1Aq$, or $(4[C^{14}H^{8}O^{8}]+5PbO)+PbO,HO$. The alcoholic liquid filtered from this lead salt was mixed with tribasic acetate of lead, which produced a yellow precipitate, which was washed with alcohol, and then decomposed under alcohol by sulphuretted hydrogen. The liquid filtered from the sulphuret of lead, freed by a gentle heat from the excess of sulphuretted hydrogen, gave, upon the addition of an alcoholic solution of acetate of lead, a beautiful lemon-coloured precipitate, which was washed with alcohol, dried at 212°, and was found to consist of $C^{28}H^{15}O^{15},3PbO=C^{14}H^{7}O^{7},2PbO+C^{14}H^{7}O^{7},PbO,HO$, corresponding to the following numbers:—

Carbon	26·21	26·26	28 = 168·00	26·34
Hydrogen	2·46	2·50	15 15·00	2·35
Oxygen	18·95	18·86	15 120·00	18·83
Oxide of lead ..	52·38	52·38	3 334·68	52·48

The aqueous decoction of the herb, mixed with neutral acetate of lead, the green precipitate collected upon a filter, washed with water, dissolved in acetic acid, the acetic solution mixed with tribasic acetate of lead in small quantity, the precipitate removed, and the liquid now completely precipitated with tribasic acetate of lead, furnished a yellow precipitate resembling chromate of lead, which, after being washed and dried at 212°, had the composition $C^{56}H^{30}O^{30}$, $9PbO=4(C^{14}H^{7}O^{7})+9PbO+2Aq$, as follows:—

Carbon.....	20·69	56 =	336·00	20·86
Hydrogen	1·83	30	30·00	1·86
Oxygen	15·47	30	240·00	14·99
Oxide of lead	62·01	9	1004·04	62·29

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The above formula may also be viewed as $2(C^{14}H^{7}O^{7}, 3PbO) + 2(C^{14}H^{8}O^{8})3PbO$.

From the above analyses it may be seen that the salts contain an acid, which consists of 14 equivs. of carbon, and contains hydrogen and oxygen in equal proportions. In order to procure the acid in the isolated state, a lead salt was suspended in water, treated with sulphuretted hydrogen, the yellow solution filtered from the sulphuret of lead, and evaporated on the water-bath in a current of carbonic acid. When the whole of the water had distilled off, the residue was removed from the retort; it formed a slightly brownish-yellow mass, with an acid astringent taste, readily soluble in alcohol and water, sparingly soluble in æther, and greedily absorbing moisture from the atmosphere. In contact with the air, the acid absorbs oxygen, and acquires a darker colour. As it still remained viscous after standing ever so long over sulphuric acid *in vacuo*, it was dried at 212°. The analysis gave—

Carbon	51·08	14 =	84	50·90
Hydrogen	5·19	9	9	5·45
Oxygen	43·73	9	72	43·65

The formula $C^{14}H^{9}O^{9}$ would represent the hydrate of the acid; the acid contained in the salts is $C^{14}H^{8}O^{8}$, from which 1 more equiv. of water can be expelled under certain circumstances. The formula of the hydrate of aspertannic acid is $C^{14}H^{8}O^{8}+HO$.

The numbers found in the above-mentioned analysis also agree pretty well with the formula $C^{14}H^{8}O^{9}$, and this composition would be explained by an incipient oxidation, $C^{14}H^{8}O^{8}+O=C^{14}H^{8}O^{9}$.

Properties of Aspertannic Acid.—A solution of this acid in water strikes with a dilute solution of perchloride of iron a dark green colour. With dilute hydrochloric or sulphuric acid and the application of heat, there is no perceptible alteration, although a decomposition of the acid takes place. On being mixed with nitrate of silver, a separation of metallic silver results. Alkalies cause the liquid to assume a brown-red colour, which becomes darker by absorption of oxygen, finally opake and blackish-brown. Albumen and solution of gelatine are not precipitated. A solution of tartar-emetic produces no precipitate; solutions of peroxide of copper cause a dark green colour. Both the neutral and the basic lead salts cause yellow precipitates.

To ascertain how far the absorption of oxygen proceeds in a solution of the acid after the addition of alkali, a concentrated aqueous solution of the acid was mixed with a solution of caustic potash, placed in a shallow dish loosely covered with paper, and exposed to the action of the air.

When no further alteration resulted in the liquid, which had become dark brown and opake, it was neutralized with acetic acid and mixed with a neutral solution of acetate of lead, when a slight reddish-brown precipitate was formed, from which the liquid was filtered, and precipitated with tribasic acetate. The gray precipitate had a slight tint of red, was collected upon a filter, and washed with

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alcohol. It was pretty readily soluble in water. Dried at 212°, it gave on analysis—

Carbon	8·69	36 =	216·00	8·80
Hydrogen	0·83	20	20·00	0·81
Oxygen	8·48	26	208·00	8·58
Oxide of lead	82·00	18	2008·08	81·81

These results may be arranged as follows:—$C^{36} H^{20} O^{26}$, 18PbO $= 2(C^{12} H^5 O^7, 5PbO) + (C^{12} H^5 O^7, 3PbO) + 5(PbO, HO)$. It is evident from these numbers that a decomposition of the acid has resulted from the action of the oxygen; $C^{14} H^8 O^8$ has become $C^{12} H^5 O^7$ or $C^{12} H^6 O^8$; consequently $C^2 H^2$ has separated in some form or the other, whilst the remainder of the atoms have continued combined with the base. This decomposition is analogous to that which caffeotannic acid experiences under the same circumstances. According to Liebich, $C^{14} H^8 O^7$, on being exposed to the action of the air with potash, passes into $C^{12} H^6 O^5$, and subsequently into $C^{12} H^5 O^6$ and $C^{12} H^4 O^7$. Kinovatannic acid changes, according to Hlasiwetz, into kinova-red, $C^{14} H^8 O^7$ furnishing $C^{12} H^6 O^5$. Consequently 2 equivs. of carbon and 2 equivs. of hydrogen appear to be contained in this acid in a different form from the other 12 equivs. of carbon and 6 equivs. of hydrogen. This elimination of 2 equivs. of carbon may also be effected by the action of dilute sulphuric acid at an elevated temperature, as will be mentioned further on. A proof of the ease with which the oxidation of aspertannic acid proceeds is afforded by its behaviour towards a solution of persalts of copper.

A solution of the pure acid was mixed with carbonate of copper, and gently heated, when a green solution of a copper salt formed; alcohol threw down a green precipitate, which was washed with alcohol and dried at 212°; it was now grayish-brown, contained 33·98 protoxide of copper, and the organic substance combined with it yielded—

Carbon	38·88	14 =	84	38·88
Hydrogen	5·43	12	12	5·55
Oxygen	55·69	15	120	55·57

Now $C^{14} H^{12} O^{15} = C^{14} H^7 O^{10} + 5Aq$. From $C^{14} H^8 O^8$, 1 equiv. hydrogen has separated, whilst 2 equivs. oxygen have been assimilated; the oxygen has been partly taken from the peroxide of copper, which has become converted into protoxide.

When an aqueous solution of aspertannic acid is mixed with moderately-dilute sulphuric acid, and kept boiling until the neutralized liquid no longer strikes a green colour with a solution of perchloride of iron, the sulphuric acid then removed by the addition of sufficient tribasic acetate of lead as sulphate of lead, a further addition of tribasic acetate produces in the filtered liquid a light yellow precipitate, which, washed upon a filter with alcohol and dried at 212°, had the composition $C^{60} H^{21} O^{21}$, 9PbO $= 4(C^{12} H^4 O^4, 2PbO) + (C^{12} H^6 O^4, PbO, HO)$:—

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Carbon.....	23·06	60	= 360·00	23·11
Hydrogen	1·48	21	21·00	1·34
Oxygen	10·52	21	168·00	10·91
Oxide of lead	64·94	9	1003·94	64·64

If we conceive the oxide of lead of the salt to be replaced by water, the formula of this body $C^{12} H^4 O^4 + 2HO = C^{12} H^6 O^6$.

The origin of this substance from aspertannic acid is explained by the following equation:—

$$C^{14} H^8 O^8 - C^{12} H^6 O^6 = C^2 H^2 O^2.$$

The group $C^2 H^2 O^2$ appears to have been eliminated as acetic acid, $C^4 H^4 O^4 = C^4 H^3 O^3 + HO$; at least no formation of sugar, or any other similar substance, was observed. In this respect the formula of aspertannic acid would range with those of caffeotannic and kinovatannic acids:—

Caffeotannic acid	$= C^{14} H^8 O^7 = C^2 H^2 O^2 + C^{12} H^6 O^5$
Kinovatannic acid	$= C^{14} H^8 O^7 = C^2 H^2 O^2 + C^{12} H^6 O^5$
Aspertannic acid	$= C^{14} H^8 O^8 = C^2 H^2 O^2 + C^{12} H^6 O^6$.

In the first of these acids, the $C^2 H^2 O^2$ would be contained as the aldehyde of formic acid; in the second as a hydrocarbon, which on its separation passes into sugar; and in the third, in the form of a compound, which on its elimination passes into acetic acid.

Aspertannic acid completes the series of acids which have been discovered in various plants of the Rubiaceæ, and examined by Rochleder and his pupils. We have at the present time—

Ipecacuanhic acid.. $C^{14} H^8 O^6 + HO$	Kinovatannic acid.. $C^{14} H^8 O^7$
Caffeotannic acid .. $C^{14} H^8 O^7$	Aspertannic acid .. $C^{14} H^8 O^8$

Rubichloric Acid.—When an aqueous decoction of the herb is mixed with neutral acetate of lead, the precipitate contains merely a trace of rubichloric acid; more occurs in that produced by tribasic acetate of lead in the liquid which has been filtered from the first precipitate; but the greatest quantity is contained along with some sugar in the precipitate produced by ammonia in the liquid which has been filtered from the precipitate obtained with tribasic acetate of lead.

This last pale yellow precipitate was washed with alcohol to remove the water, then mixed with anhydrous alcohol, and decomposed by sulphuretted hydrogen. The solution filtered from the sulphuret of lead was gently heated to remove the excess of sulphuretted hydrogen, then mixed with an alcoholic solution of acetate of lead to which a few drops of ammonia had been added. The white precipitate which is formed is dried *in vacuo* over sulphuric acid and caustic potash; in this operation it becomes yellow and transparent, but furnishes a perfectly white powder. Analysis led to the formula $C^{42} H^{30} O^{33}, 8PbO = 3(C^{14} H^{10} O^{11}) + 8PbO = 3(C^{14} H^8 O^9) 2PbO + 6PbO, HO$:—

Carbon.....	17·56	42	= 252·00	17·51
Hydrogen	2·09	30	30·00	2·68
Oxygen	18·27	33	264·00	18·37
Oxide of lead	62·08	8	892·48	62·04

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The analyses by Willigk and Rochleder of rubichloric acid, obtained from the herb and the root of *Rubia tinctorum*, gave the same results. An aqueous solution of this substance, mixed with hydrochloric acid and heated in the water-bath, yields formic acid and a green flocculent precipitate of chlorrubine, which was collected on a filter, washed with water, and dried for analysis *in vacuo*. It furnished—

Carbon	61·17	12 =	72	61·01
Hydrogen	5·07	6	6	5·08
Oxygen	33·76	5	40	33·91

Chlorrubine is produced in the following manner:—

$C^{14} H^8 O^9$, rubichloric acid, $-C^2 H^2 O^4 = C^{12} H^6 O^5$, chlorrubine.

This green substance cannot be dried at 212°, as it changes its colour, and it is evident from analysis that it has absorbed oxygen. It dissolves in a solution of caustic potash and ammonia with a beautiful red colour, and is again precipitated from these solutions by acids.

Citric and Catechuic Acids.—When the aqueous decoction of the herbaceous part of *Asperula odorata* is precipitated with a solution of acetate of lead, there is formed, as previously stated, a dirty green precipitate, which partially dissolves when left some time in contact with acetic acid. The portion not dissolved by the acetic acid is mixed with water, decomposed with sulphuretted hydrogen, and filtered from the sulphuret of lead, when it furnishes a yellowish solution containing phosphoric and sulphuric acids, and also the organic acids of *Asperula*, of aspertannic acid but little, rather more of a second acid, and but a small quantity of a third, which appears to be citric acid. The liquid was divided into three portions; to one a solution of neutral acetate of lead was added as long as any precipitate was produced, and then the two other portions mixed with it. After long digestion, the precipitate, consisting for the greater part of phosphate and sulphate of lead, was separated, the filtered liquid completely precipitated with neutral acetate of lead, the precipitate dissolved in acetic acid, when a small portion remained undissolved, and the solution precipitated by tribasic acetate of lead. This precipitate, washed with alcohol and dried at 212°, had the following composition:—$C^{56} H^{31} O^{49}$, $13PbO = 2(C^{12} H^5 O^{11}, 3PbO) + (C^{12} H^5 O^{11}, HO, 2PbO) + 5(C^4 H^3 O^3, PbO)$:—

Carbon.....	15·25	56 =	336·00	15·21
Hydrogen	1·55	31	31·00	1·40
Oxygen	17·67	49	392·00	17·74
Oxide of lead ..	65·53	13	1450·28	65·65

This composition agrees with that of a salt which was prepared by Rochleder and Willigk from the herb and root of *Richardsonia scabra*.

The authors however could not succeed in obtaining the citric acid in a crystalline state, while in the case of *Richardsonia scabra*

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it was procured in well-developed crystals. However, the liquid obtained by decomposing the above salt by sulphuretted hydrogen exhibited all the reactions of a solution of citric acid.

When the aqueous decoction of *Asperula* is precipitated with neutral acetate of lead, the precipitate digested in acetic acid, the acid solution mixed with basic acetate of lead, and the precipitate produced upon the addition of the first few drops collected apart, a yellow salt is obtained, which turns green on being dried at 212°, whilst the next following precipitate of aspertannate of lead retains its colour unaltered. In the following, the results of the analyses of several lead salts prepared in this manner are given:—

I. Formula, $C^{42} H^{20} O^{20}$, $4PbO = 2(C^{14} H^7 O^7, PbO) + (C^{14} H^6 O^6, 2PbO)$.

Carbon.....	28·86	42	= 252·00	28·69
Hydrogen	2·44	20	20·00	2·26
Oxygen	18·18	20	160·00	18·24
Oxide of lead ..	50·52	4	446·24	50·81

II. The organic substance in a second lead salt, after deducting the oxide of lead, leads to the following formula:—

$C^{42} H^{19} O^{19} = 2(C^{14} H^6 O^6) + C^{14} H^7 O^7$.

Carbon.....	59·43	42	= 252	59·57
Hydrogen.....	4·53	19	19	4·49
Oxygen.....	36·04	19	152	35·94

Catechuic acid or catechine has the formula $C^{14} H^8 O^3 = C^{14} H^6 O^6 + 2HO$; the lead salts of catechine possessed the property of turning green. The salts enumerated might, from their composition, be viewed as mixtures of aspertannate and catechuate of lead, but the author was unable to prepare crystallized catechine or catechuic acid from them; the greatest difficulty was owing to the small quantity of the acid contained in the plant. The author then attempted to prepare pyrocatechine by destructive distillation of the acid mixture; no crystallized pyrocatechine was obtained, but a liquid, the reactions of which with persalts of iron, alkalies, bichloride of platinum, nitric acid, and acetate of lead render probable the presence of pyrocatechine. The two principal constituents, the aspertannic and rubichloric acids, stand in a very simple relation to each other as regards their constitution and mode of decomposition, as already stated:—

Aspertannic acid, $C^{14} H^8 O^8 = C^2 H^2 O^3 + C^{12} H^6 O^6$,
Rubichloric acid, $C^{14} H^8 O^9 = C^2 H^2 O^4 + C^{12} H^6 O^9$.

Bericht der Wiener Academie.

On the Preparation of Caffeine. *By* H. J. Versmann.

The author mixes the powder of 10 lbs. of coffee with 2 lbs. of caustic lime, which is previously converted into hydrate by being sprinkled with water. The mixture is placed in a displacement ap-

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paratus, and exhausted with alcohol of 0·863 until a sample of the liquid which passes no longer shows the presence of caffeine on evaporation. As coffee is exceedingly difficult to pound, and much depends upon the degree of fineness of the powder, the residue, after one treatment with alcohol, is removed from the displacement apparatus, dried, and pounded again, mixed with hydrate of lime, and extracted again. It is now more readily pounded, because the coffee has lost its horny nature by the treatment with alcohol, and there is no difficulty in completely exhausting the coffee. The clear spirituous extracts obtained in this manner are submitted to distillation, the residue in the still rinsed out with warm water, and the supernatant oil separated. The liquid is then concentrated until it solidifies in the cold into a crystalline mass, which is brought upon a close strainer, and freed as much as possible by pressure from the liquid, which on evaporation furnishes some more caffeine. When the impure caffeine has been freed as much as possible by pressure between blotting-paper from adherent oil, it is purified by dissolving it in water with the addition of a little animal charcoal and recrystallization, and the preparation obtained in this manner in dazzling white crystals of a satiny lustre. The author obtained from 5 lbs. of coffee in general not more than 3 drms., from 10 lbs. 7 drms., and from 100 lbs. the largest amount, namely, 6 oz. and 4 scruples of caffeine. According to this, good Brazilian coffee contains 0·57 per cent. of caffeine. At the same time the author obtained on an average 10 per cent. of a green liquid oil and 2 per cent. of a yellow solid fat.—*Archiv der Pharm.*, lxviii. p. 148.

On the Production of Chloroform from Chloride of Lime and the Essential Oil of Turpentine. By J. CHAUTARD.

On mixing intimately in a retort 600 parts of water, 200 parts of chloride of lime and 25 of oil of turpentine, and submitting the mixture to distillation, a violent reaction occurs, and at the same time a very agreeable ætherial odour is manifested. A large quantity of carbonic acid gas is disengaged, which, as it causes the matter to froth, necessitates the employment of large vessels. On removing the retort from the fire as soon as the mixture begins to rise, the operation goes on well, and continues of itself to the end. The receiver contains three layers, frequently intermixed. The first consists of essential oil, which appears to have escaped the reaction; the lower one is an ætherial liquid, with the odour of chloroform; the intermediate layer consists of water, holding in solution a considerable amount of the preceding product. The latter is separated by means of a pipette, and rectified on the water-bath; two or three treatments of chloride of calcium and a few fractionated distillations suffice to render it perfectly pure.

This product presented all the properties and the composition of the chloroform of the methylic series. It is a perfectly colourless, highly mobile liquid, with a very sweet taste and a most agreeable odour, heavier than water, in which it dissolves perceptibly, com-

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municating to it the two preceding properties; it boils at 145°·4 F. On analysis it furnished C 10·47, H 1·05, Cl 88·59; theory requires C 10·05, H 0·84, Cl 89·11.

The slight excess of carbon and hydrogen obtained must, I think, be attributed to a small quantity of carburet of hydrogen, which tenaciously accompanies the chloroform, and from which it might perhaps be freed by distillation over sulphuric acid. This would at the same time account for the few degrees of difference between the boiling-point of the substance under consideration and that admitted for chloroform.

I have no doubt that, by modifying the above process, we shall succeed in obtaining chloroform at far less expense than by the method of preparation generally in use.—*Comptes Rendus*, Dec. 15, 1851.

On the Allotropy of Selenium. *By* M. Hittorf.

It is well known that selenium is softened by heat, becomes semi-fluid at 212°, and melts at a few degrees higher. In cooling, it becomes viscous, thickens more and more, like wax, and then solidifies into a reddish mass, with a shining surface and a conchoidal and vitreous fracture. Berzelius had already observed, that when the cooling takes place very slowly, the selenium acquires a reddish colour, a rough surface, a dull granular fracture, but that it loses this appearance when it is melted again and cooled rapidly.

The author having attentively studied these phænomena, has found that they are due to the existence of an allotropic modification of selenium analogous to that presented by sulphur, and evidenced by the fact that the crystallized selenium melts without any previous softening, but at a temperature of 422°·6 F.

When the substance is melted and the temperature raised, for instance to 428°, and left to cool with a thermometer immersed in it, the temperature is seen to descend gradually without the thermometer becoming stationary, without its even being possible to observe a single point where its cooling appears to slacken until it has attained the temperature of the medium. At the same time the selenium passes through all degrees of viscosity until at about 122° it entirely solidifies into a resinous mass. In these circumstances the substance has therefore solidified in the amorphous state without having lost its latent heat of fusion; and it may retain it indefinitely, for it persists in this amorphous state at the ordinary temperature. But it passes into the crystalline state when kept for some time at a temperature between 176°–422°, and it then parts with its latent heat.

Between 176° and 212° the transformation requires several hours; and in this case the disengagement of heat which accompanies it is not appreciable. Between 257° and 356° it is very rapid; and if we operate upon 20 grms. of selenium, which are heated in an oil-bath, a thermometer immersed in the interior of the substance, after having attained the temperature of the bath, will rapidly exceed it,

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and will rise from 70° to 90° above it for some minutes. This phænomenon is still more striking when a hot air-bath is substituted for an oil-bath. In one experiment, in which the bath was heated to 266°, the author observed the thermometer, after having risen slowly to 257°, ascend suddenly to between 410° and 419°.

When the selenium is employed in the state of powder, its metamorphosis is more rapid. In this case, even in a bath heated merely to 212°, the crystalline state may be developed so rapidly that the heat rises from 45° to 52° above that of the interior.

These phænomena are exactly similar to those which are presented by sulphur. When this substance is strongly heated, and it is then suddenly cooled, it is converted into an amorphous, soft and elastic mass. At the ordinary temperature it passes gradually, but very slowly, from this amorphous state into the hard and crystalline state in which it is ordinarily met with. At a temperature approaching 212°, it passes in a few minutes into this state; and it is well known that M. Regnault noticed in this case the temperature of the soft sulphur rise spontaneously to 232° in a chamber heated to 208°. The only difference which exists between these two bodies is, that with sulphur the ordinary temperature is sufficiently near that at which the change of state takes place for the transformation to be gradually effected; whilst in the case of selenium, it is requisite to raise it to a more elevated temperature in order to cause it to pass from the amorphous into the crystalline state.

In many chemical reactions the selenium is separated from its solutions in the form of an amorphous red powder. It is obtained thus by precipitating selenious acid by sulphurous acid, by the chlorides of tin, zinc, iron, or by exposing a solution of hydroselenic acid to the atmosphere, or by diluting with water a solution of amorphous or crystallized selenium in concentrated sulphuric acid. These precipitates have only to be exposed to the action of the solar rays to make them gradually pass into the crystalline state.

In other circumstances selenium may be precipitated at the ordinary temperature in the crystalline state; for instance, when solutions of seleniuret of potassium or ammonium are exposed to the air.

Selenium exhibits very different densities in its two allotropic modifications. In its amorphous state the specific gravity is 4·26–4·28, whilst in the crystalline it is 4·80; its conductibility for electricity likewise varies considerably; the vitreous selenium insulates almost perfectly, whilst the crystalline substance is a very excellent conductor. In this state it exhibits a very curious phænomenon, that of the resistance decreasing in proportion as the temperature rises, provided its point of fusion be not attained.

The author concludes his memoir by some observations on the analogy which exists between the phænomena of allotropy presented by sulphur and selenium and that which M. Schrœtter has published regarding phosphorus; he thinks that the latter chemist commits a mistake in considering the red phosphorus as amorphous; and although we have not yet been able to obtain this modification in the crystalline state, he believes that it is the state of phosphorus

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corresponding to the crystalline sulphur and selenium, and that very probably this body, in passing into that state, likewise disengages a quantity of heat.—Poggendorff's *Annalen*, lxxxiv. p. 214.

On a Process for detecting the Presence of Water in various Substances. *By* A. Gorgue.

The presence of water in the alcohols and æthers may readily be detected by taking advantage of the property they possess of rendering benzine turbid when they contain water.

The only condition requisite for ascertaining the presence of water in a liquid is, that it must be soluble in the benzine. The following is the plan of operating, for instance, with alcohol:—It suffices to pour *one single drop* into 3–4 cub. centims. of benzine. If the drop falls to the bottom of the tube in which the experiment is made without producing any turbidity, the alcohol contains more than a third of its weight of water. To be convinced that the alcohol contains too much water for any opakeness to be produced, it suffices to add some absolute alcohol to a small quantity of the liquid, and to repeat the experiment. Every time that there is a production of turbidness, accompanied with the formation of little globules, we may be certain that the strength of the alcohol will be comprised between 65 and 93 centesimal degrees. If but a cloudiness be produced, the liquid contains at the most seven-hundredths of water. In this case the opacity may be made to disappear by the addition of some stronger alcohol. The experiment is made with benzine saturated with water, in little short dry tubes closed at one end, and of about 12 millims. in diameter.

When an æther is to be examined, essential oil of turpentine is preferable to benzine, as the turbidness produced is more persistent. It is not employed to detect the water in the alcohols, from its being less sensitive than benzine; in fact, an alcohol of 98° no longer renders it turbid.

By operating as I have stated, from seven- to eight-thousandths of water can be readily detected in an alcohol, and from three- to four-thousandths in an æther.

Any substance soluble both in the liquid under examination (alcohol, æther, &c.) and in the test for water (benzine, essential oil of turpentine, &c.) does not affect the sensitiveness of the process, which however is impracticable whenever one of the first liquids holds in solution a substance insoluble in the latter.

The property which hydrated æther possesses of rendering the oil of turpentine opake, may be applied to determine the hygrometric water in salts. It suffices to leave them in contact for a few minutes with anhydrous æther, and then ascertain whether it renders turpentine turbid. This mode of operating cannot be adopted in the case of substances insoluble in the turpentine which dissolve in the æther, or of salts which are dehydrated by the latter liquid, for instance, very efflorescent salts, such as the crystallized phosphate, carbonate and sulphate of soda. The process may be applied

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for detecting the presence of interstitial water in the slightly-efflorescent crystalline salts, as the sulphate of copper and the sulphate of manganese, and those which are unaltered by exposure to the air, as the chloride of barium, the oxalate of ammonia, &c. Æther is preferable to alcohol in these experiments, because a smaller proportion of water can be discovered in it; and, moreover, the latter liquid dissolves, and dehydrates a larger number of salts than æther.

Taking advantage of the insolubility of water in benzine, I have been able to preserve intact, crystals of deliquescent salts, as those of the chloride of calcium and bichloride of copper; efflorescent salts, as the phosphate, sulphate and carbonate of soda; and lastly, crystals of salts which become oxidized in the air in the course of time, as the protosulphate of iron. To preserve these substances in benzine, it is only requisite that they should have been well dried on blotting-paper or wiped with a piece of fine linen. Crystals which had been kept in benzine lost all smell after they had been submitted for a short time to a somewhat brisk current of air, and had experienced no alteration in their composition or properties.—*Comptes Rendus*, Dec. 22, 1851.

On the Existence of Organic Matter in Stalactites and Stalagmites, forming Crystallized and Amorphous Crenate of Lime. By David A. Wells.

In the eighth chapter of Liebig's Agricultural Chemistry, edited by Playfair, there is given the result of some examinations of stalactites from caverns in Germany, and from the vaults of old castles upon the Rhine, made with the view of ascertaining the fact of the presence or absence of organic matter in these bodies, either combined or uncombined.

The result may be stated in the words of the author, Prof. Liebig. The stalactites from the caverns "contain no trace of vegetable matter, and no humic acid, and may be heated to redness without becoming black." In the stalactites from the vaults and cellars of old castles, he says, "we could not detect the smallest traces" of humic acid. "There could scarcely be found a more clear and convincing proof of the absence of the humic acid of chemists in common vegetable mould." Under the term humic acid, Prof. Liebig undoubtedly means to include all those organic acids arising from the decomposition of vegetable matter, and which have received the names of crenic, apocrenic, geic and humic acids.

Having been informed by Dr. A. A. Hayes of Boston, that he had in numerous examinations arrived at results directly opposed to those of Prof. Liebig, I was induced at his suggestion to make an examination of a large number of stalactites and stalagmites obtained from various localities, with reference solely to the presence or absence of organic matter in these bodies.

The specimens examined were all from caverns, or rock formations, and were obtained from various parts of the United States, from Trieste in Austria, Malta and the Sandwich Islands. In colour

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they varied from an almost pure white to red, yellow, and brown of different shades; and in crystalline character, from a structure resembling arragonite to a variety entirely wanting in symmetrical arrangement, or a mere incrustation. The specimens were dissolved in dilute hydrochloric acid, the flocculent matter separated, collected and washed, boiled in caustic potash, carbonate of ammonia or carbonate of soda, and then tested in the usual way for crenic and apocrenic acids by acetate of copper and carbonate of ammonia. In all the varieties, with one exception, abundant flocculent organic matter was separated, which on testing gave evidence of crenic acid in considerable quantities, with doubtful traces of apocrenic acid. The exception alluded to was the specimen examined from Trieste, which did not afford any appreciable flocculent matter on dissolving in acid. The greatest quantity of organic matter was found in stalactites of a deep yellow colour, highly crystalline and uniform in character, and in the portions examined perfectly homogeneous and free from layers, or intervening bands indicating different periods and changes in deposition. As the presence of iron could not be found in the acid solution, it is inferred that the colour of these yellow stalactites must be owing in great part to combined organic matter, existing as crenate of lime. In specimens like the spar ornaments from the Rock of Gibraltar, with which all are familiar, the colouring and delicate shading is also probably due to organic matter.

Dr. Hayes informs me, that he has also found organic matter in arragonite in sufficient quantity to separate in flakes, while the specimen was dissolving in acid.

From these statements, it must, I think, be inferred, contrary to the view of Liebig, that organic matter does exist in stalactites generally, as an acid combined with the lime, and imparting to them their various colours. I would by no means call in question the accuracy of the experiments of Prof. Liebig, further than that, as far as my observations extend, crenic acid in the presence of lime, and combined with it, passes over like oxalates, upon heating, into carbonates, without perceptible blackening.

It may here be added, that Prof. Johnston of England describes a compound of alumina with crenic acid, occurring in caves of granite upon the coast of Cornwall. This mineral has received the name of Pigotite, and is observed in places where the surface-water trickles down over the granite rocks. From this it may not be inappropriate to apply the term *crenite* to those lime formations in which crenic acid occurs in considerable quantities.

Results similar to those announced above have been obtained by Dr. C. T. Jackson, as well as by Dr. Hayes of Boston. Dr. J. Lawrence Smith informs me, that he has frequently met with crenic acid in lime concretions from Asia Minor, and its existence in stalactites was also announced by Dr. Emmons of Albany some years since. My results can therefore be considered but as the verification of those obtained by others.—Silliman's *Journal*, Jan. 1852.

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On the Solubility of Chloride of Silver in the Pernitrate of Mercury. By Prof. LIEBIG.

In preparing the compound of urea and peroxide of mercury, described in page 37 of the present volume of this Journal, a solution of perchloride of mercury was mixed with a solution of urea to which some caustic potash had been previously added. The snow-white precipitate was washed with water until a portion dissolved in nitric acid remained perfectly clear on being mixed with nitrate of silver. The same reaction being exhibited by the wash-water, the compound was considered to be free from chlorine, as not a trace could be detected by the usual test for that substance.

However, on analysing the compound, it was evident that it contained some other substance besides urea and peroxide of mercury; and on closer examination it was found to contain a considerable amount of chlorine, which had not been indicated by the oxide of silver. It was ascertained that the compound of urea and oxide of mercury, dissolved in nitric acid and mixed with a solution of silver, furnished, on the addition of a solution of corrosive sublimate, or any other chloride, a precipitate, which differed by its pulverulent nature from chloride of silver, and dissolved entirely when the liquid was boiled. It was further found that the presence of urea has no influence upon this behaviour, and that chlorine is not precipitated by silver in the presence of nitrate of mercury. In fact, as long ago observed by Wackenroder, chloride of silver dissolves in a warm solution of the above salt to a considerable amount; and the solution deposits, upon the addition of water and cooling, shining yellowish-white crystals, which consist of pure chloride of silver. Alkaline acetates, added to the solution of the chloride of silver in the pernitrate of mercury, precipitate chloride of silver.—Liebig's *Annalen*, Jan. 1850.

On the green Colouring Matter of Plants, and on the red Matter of Blood. By F. VERDEIL.

The green matter which can be extracted from the majority of plants by means of alcohol or æther was considered as a pure homogeneous organic substance, and received the name of *chlorophylle*, or green resin of plants.

I have discovered that this green resin is a mixture of a perfectly colourless fat capable of crystallizing, and of a colouring principle presenting the greatest analogies with the red colouring principle of the blood, which however had never yet been obtained in a completely pure state.

To isolate it, I precipitate a boiling solution of chlorophylle in alcohol by a small quantity of milk of lime. The solution becomes colourless, the alcohol retains the fat, whilst the lime precipitates all the colouring matter. This is separated from the lime by hydrochloric acid and æther, which dissolves the green matter, forming a coloured stratum at the top of the liquid. By evaporating the æther, the colouring matter is obtained in a state of perfect purity.—*Comptes Rendus*, Dec. 22, 1851.

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CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Estimation of the Amount of Peroxide of Manganese and available Chlorine in Commercial Oxide of Manganese and Bleaching Powder. *By* Dr. L. Müller.

There are few substances used in the arts for which so many valuation tests have been proposed as the peroxide of manganese, and yet the operator would find the want of a method suitable to this purpose which combined easy execution with a sufficient degree of accuracy. The author considers that he has supplied this deficiency by the adoption of the following method. It is founded upon the reducing action exercised by protochloride of tin upon a number of bodies, converting oxides to suboxides, chlorides to subchlorides, and particularly of converting perchloride of iron into protochloride, while passing itself, entirely or partially, into perchloride of tin. It is easy to recognise this action of the protochloride of tin upon perchloride of iron by the change of colour which a solution of the latter experiences on the addition of the former; the brown, brownish-yellow, and yellow colours of the perchloride of iron gradually disappear, and at length a colourless or faint green solution remains, in which all the iron is contained as protochloride. The change of colour may be rendered still more striking to the eye by the addition of a few drops of a solution of sulphocyanide of potassium to the solution of perchloride of iron before the experiment; sulphocyanide of iron is formed in this case, which communicates to the solution an intense dark red colour, which disappears on the addition of a sufficient quantity of protochloride of tin.

The fact is now evident, to which attention had already been directed by Prof. Schulze of Rostock, that this mutual reaction of protochloride of tin and perchloride of iron may be taken advantage of for the analysis of a solution of one of these salts by a solution of the other, in which the proportion of salt is known; for in order that, after the mixture, only perchloride of tin and protochloride of iron may be present, there must have been, before the mixture, a definite relation between the quantities of protochloride of tin and perchloride of iron. Thus there results from

$$SnCl \text{ and } Fe^2Cl^3$$
$$SnCl^2 \text{ and } Fe^2Cl^2 = 2FeCl, \text{ or}$$

1178·574 protochloride of tin and 1990·894 perchloride of iron give 1621·854 perchloride of tin and 1547·614 protochloride of iron.

In order to derive advantage from this behaviour of protochloride of tin and perchloride of iron, two courses might be followed. First, a solution of protochloride of iron might be converted into perchloride by the action of the chlorine developed from hydrochloric acid by the oxide of manganese to be valued, and then the quantity of

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perchloride of iron thus formed in this solution determined by means of a solution containing a known proportion of protochloride of tin. This proceeding, however, is not practically applicable, since chlorine is not absorbed by a solution of protochloride of iron with sufficient rapidity to obviate all loss. By the second method, the chlorine evolved may be passed through a solution of protochloride of tin, and the perchloride produced estimated by means of a solution of perchloride of iron of known strength. This second method has proved perfectly applicable in practice, as the chlorine is rapidly and completely absorbed by a solution of protochloride of tin.

The following is the mode of conducting the examination:—A solution of perchloride of iron, free from nitric acid and uncombined chlorine, is tested to determine its per-centage of perchloride, by precipitating in the usual way the iron from 50 cub. centims. of the solution by means of ammonia, and determining the quantity as peroxide. Such a solution, chemically pure and of known strength, is, as we shall soon see, necessary only in the first instance. Next, protochloride of tin is dissolved in water, and hydrochloric acid added until the solution becomes quite clear. This solution is added drop by drop to 50 cub. centims. of the solution of perchloride of iron (to which a few drops of sulphocyanide of potassium have been added) until the colour disappears. In this way the quantity of protochloride of tin in a given quantity of the solution is ascertained; for supposing the solution of perchloride of iron contains in 50 cub. centims. 19·9 grms. of perchloride, there would be 11·78 grms. of protochloride of tin in the quantity of solution employed. This calculation of the quantity of salt in the solution of protochloride of tin is however unnecessary in the valuation of oxide of manganese when the number of degrees is known which are requisite for the reduction of a certain quantity of perchloride of iron into protochloride; it is however indispensable to test the solution of protochloride of tin before each valuation of oxide of manganese, in consequence of its tendency to form, by the absorption of oxygen, a basic salt, which precipitates. After this preliminary examination, a double quantity of the solution of protochloride of tin is poured into a tube which is graduated into 200 half parts, the tube filled to about 90 with water, and then the chlorine developed by a determinate quantity of oxide of manganese passed through it. The quantity of the oxide of manganese to be used in the valuation is regulated by the concentration of the solution of perchloride of iron; and indeed so much oxide must always be used for the examination, that if it were pure peroxide of manganese, it would set free as much chlorine as would be evolved by 50 cub. centims. of the solution of perchloride of iron in its conversion into protochloride. Or as 1 milligrm. of perchloride of iron ($Fe^2 Cl^3$) evolves 1 milligrm. of chlorine in passing into protochloride; further, 1 milligrm. of peroxide of manganese (MnO^2) is also capable of developing 1 milligrm. of chlorine; consequently the quantities of perchloride of iron and oxide of manganese must always be in the same proportion to each other as their equivalents. If therefore 50 cub. centims. of the

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solution of perchloride of iron contain a grms. of perchloride, then the formula

$$1990{\cdot}894 : 544{\cdot}684 :: a : x$$

$$x = \frac{544{\cdot}684 \cdot a}{1990{\cdot}894} = 0{\cdot}274\, a$$

gives the quantity of oxide of manganese to be employed.

This quantity of oxide is introduced into a small glass flask, in the neck of which a tube is inserted by means of a well-fitting cork, the requisite quantity of hydrochloric acid added, the mixture moderately warmed in a sand-bath, and the chlorine evolved led into the solution of protochloride of tin; after the evolution of gas has ceased, the conducting tube is removed from the tin solution, water added to this up to the hundredth-part mark, and then examined to ascertain how many parts of this solution (acted on by chlorine) are necessary in order to again convert 50 cub. centims. of the solution of perchloride of iron (after the addition of a few drops of sulphocyanide of potassium) into protochloride of iron. How the per-centage of peroxide of manganese in the commercial oxide is calculated from the number of parts of this altered tin solution that are used, will readily be seen from the following consideration:—Since this tin solution originally contained twice as much protochloride of tin as was necessary for the reduction of the perchloride of iron contained in 50 cub. centims. of the iron solution, it is evident that the commercial oxide would contain 0 per cent., or no peroxide at all, when only half the altered tin solution, or 50 parts, should have been consumed in effecting this change; if however more were required, it would be because a part of the protochloride of tin was converted into perchloride by the action of the chlorine evolved, and consequently the solution rendered weaker in reference to the protochloride of tin; and it is equally obvious that 100 parts consumed represent 100 per cent. of peroxide of manganese. The per-centage of peroxide represented by the quantities of solution between 50 and 100 parts is ascertained by simple calculation. Let n be the number of parts used; now these contain just as much protochloride of tin as 50 parts of the unaltered solution, and the quantity of protochloride in the altered solution is to that in the unaltered as 50 to n, or the former is equal to $\frac{50}{n}$ of the latter; consequently the quantity of the perchloride of tin found amounts to $\frac{n-50}{n}$, or in per-cents. of the whole quantity $100\,\frac{n-50}{n}$; since however the quantity of the commercial oxide used, even in the best samples, could only convert half of the protochloride of tin into perchloride, the quantity of perchloride of tin formed must be calculated as per cents. of half the tin solution, and there is obtained for this $200\,\frac{n-50}{n}$,

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which are at the same time the per-centages of peroxide of manganese. Thus, for example, if 62·5 parts of the altered solution have been used in order to convert 50 cub. centims. of solution of perchloride of iron into protochloride, the commercial oxide of manganese will contain $200 \cdot \frac{62{\cdot}5-50}{62{\cdot}5} = 200 \cdot \frac{12{\cdot}5}{62{\cdot}5} = 40$ per cent. of peroxide of manganese. The following table obviates the necessity of this calculation:—

TABLE *showing the per-centage amount of Peroxide in a Manganese when the quantities used in the examination are as* 1990·894 *perchloride of iron* : 2357·148 *protochloride of tin* : 544·684 *manganese.*

No. of degrees of tin solution consumed.	Per-cents. of peroxide of manganese.	No. of degrees of tin solution consumed.	Per-cents. of peroxide of manganese.	No. of degrees of tin solution consumed.	Per-cents. of peroxide of manganese.	No. of degrees of tin solution consumed.	Per-cents. of peroxide of manganese.
50	0·00	62·5	40·00	75	66·66	87·5	85·70
50·5	1·98	63	41·26	75·5	67·54	88	86·36
51	3·92	63·5	42·50	76	68·42	88·5	87·00
51·5	5·84	64	43·75	76·5	69·28	89	87·64
52	7·68	64·5	44·96	77	70·12	89·5	88·26
52·5	9·52	65	46·14	77·5	70·96	90	88·88
53	11·32	65·5	47·32	78	71·78	90·5	89·50
53·5	13·14	66	48·48	78·5	72·60	91	90·10
54	14·82	66·5	49·62	79	73·40	91·5	90·70
54·5	16·50	67	50·74	79·5	74·20	92	91·30
55	18·18	67·5	51·84	80	75·00	92·5	91·88
55·5	19·82	68	52·94	80·5	76·02	93	92·46
56	21·42	68·5	54·00	81	76·54	93·5	93·06
56·5	23·00	69	55·06	81·5	77·32	94	93·62
57	24·56	69·5	56·10	82	78·04	94·5	94·18
57·5	26·08	70	57·14	82·5	78·78	95	94·72
58	27·58	70·5	58·14	83	79·52	95·5	95·28
58·5	29·06	71	59·14	83·5	80·24	96	95·82
59	30·50	71·5	60·14	84	80·94	96·5	96·38
59·5	31·92	72	61·10	84·5	81·42	97	96·90
60	33·32	72·5	62·20	85	82·34	97·5	97·42
60·5	34·70	73	63·00	85·5	83·04	98	97·94
61	36·06	73·5	63·94	86	83·72	98·5	98·46
61·5	37·38	74	64·86	86·5	84·38	99	98·98
62	38·70	74·5	65·76	87	85·28	99·5	99·50
						100	100·000

The manipulation in this valuation of commercial oxide of manganese is so simple, and its advantages over all others so obvious,

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that a more especial indication appears superfluous*; and it will therefore suffice to mention here, that the detailed analysis of the solution of perchloride of iron is necessary only at the commencement of such examinations. If, for example, the composition of a solution of perchloride is known, it is easy to determine the quantity of perchloride in a second solution by simply converting equal quantities of both into protochloride by means of the same tin solution; the quantities of perchloride of iron will be directly as the necessary quantities of tin solution. If for this purpose 50 cub centims. of the solution of perchloride of iron are employed, it is only requisite to multiply the quantity of perchloride found in the new solution by 0·274 in order to obtain the quantity of commercial oxide to be used in the examination.

We now proceed to the application of the protochloride of tin to the determination of the quantity of available chlorine contained in bleaching powder. After the preceding remarks, this may be very briefly stated. A solution of protochloride of tin is again tested by means of a solution of perchloride of iron of known strength; double the quantity that was necessary to convert 50 cub. centims. of the solution of perchloride of iron into protochloride is poured into a tube divided into 100 parts; to this is immediately added the solution of a determinate quantity of bleaching powder, and the tube filled with water up to the 100dth mark. The otherwise bleaching chlorine here effects the formation of perchloride of tin, the quantity of which is again easily determined by the solution of perchloride of iron. Bleaching powder, even the best, does not contain more than 30 per cent. of available chlorine; however, in the following table a bleaching powder with 50 per cent. is assumed partly as a standard of comparison, for the purpose of using it for other bleaching salts, partly in order to obtain suitable data for the per-centages lying between 20 and 30; 443·28 chlorine must therefore be considered as 50 per cent., and thence the quantity of bleaching powder calculated which is capable of converting an equal quantity of protochloride of tin into perchloride, as is 1990·894 perchloride of iron, whence the number 886·56. The quantity of the bleaching powder to be used in each case is consequently calculated from the quantity a of the perchloride of iron contained in 50 cub. centims., by means of the proportion

$$1990{\cdot}894 : 886{\cdot}56 :: a : x$$

$$x = \frac{886{\cdot}56}{1990{\cdot}894}\, a = 0{\cdot}446\, a.$$

* The method of the author for estimating the value of commercial oxide of manganese is ingenious and accurate, and may admit of application in many cases; it has however no advantage over the ordinary methods of valuation, especially that of Will and Fresenius; it does not surpass that either in simplicity or accuracy. With regard to the determination of the quantity of bleaching chlorine in bleaching powder, a normal solution of protoxide of iron, whose quantity of protoxide is determined, after the addition of a known quantity of the solution of bleaching powder, by Marguerite's method (Chem. Gaz., vol. v. p. 216), is at once more simple, and gives more accurate results.—Liebig.

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It is again evident, from the quantities of the individual substances selected, that in the valuation of the mixed solution of protochloride of tin and bleaching powder by 50 cub. centims. of solution of perchloride, 50 parts represent 0, and 100 parts 50 per cent. of chlorine; but the calculation of the per-centage from the consumption of parts between 50 and 100 is effected by the formula

$$100\frac{n-50}{n}.$$

In the following table this calculation is carried out for each individual part:—

TABLE *showing the per-centage amount of effective Chlorine in a Chloride of Lime when the quantities used in the examination are as* 1990·894 *perchloride of iron* : 2357·148 *protochloride of tin* : 886·56 *chloride of lime.*

No. of degrees of tin solution consumed.	Per-centage of effective chlorine.	No. of degrees of tin solution consumed.	Per-centage of effective chlorine.
50	0	76	34·210
51	1·960	77	35·065
52	3·846	78	35·897
53	5·660	79	36·708
54	7·407	80	37·500
55	9·090	81	38·271
56	10·714	82	39·024
57	12·280	83	39·759
58	13·793	84	40·476
59	15·254	85	41·176
60	16·666	86	41·860
61	18·032	87	42·528
62	19·354	88	43·181
63	20·634	89	43·820
64	21·875	90	44·444
65	23·076	91	45·054
66	24·242	92	45·760
67	25·373	93	46·236
68	26·470	94	46·808
69	27·536	95	47·368
70	28·571	96	47·916
71	29·577	97	48·453
72	30·555	98	48·979
73	31·506	99	49·494
74	32·432	100	50·000
75	33·333		

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THE CHEMICAL GAZETTE.

No. CCXXV.—March 1, 1852.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Examination of some Products derived from Hippuric Acid.

By N. Socoloff *and* A. Strecker.

As previously shown by M. Strecker, hippuric acid, when treated with nitrous acid, disengages nitrogen like other amidogen compounds, and yields a new acid, $C^{18} H^8 O^8$, which the authors have examined more minutely, and have called benzoglycolic acid.

Benzoglycolic Acid is prepared from hippuric acid by forming it into a paste with nitric acid, and passing a current of nitric oxide into it. As soon as the change is effected, water is added, and when perfectly cold, the crystals of the benzoglycolic acid collected, washed with water, the lime salt prepared from it by saturating with milk of lime, and this decomposed, after purification, with hydrochloric acid, in order to obtain the pure acid. The mother-liquor, which, after separating the crude benzoglycolic acid, still contains a considerable amount of this acid, is therefore saturated with potash, and the nitre crystallized out. The benzoglycolate of potash formed is decomposed with concentrated nitric acid, and the eliminated acid collected. It has still to be separated from some benzoic acid, which is mixed with it. For this purpose, the one-half of the impure acid is saturated with lime, the other half mixed with it, and the whole evaporated to dryness. As the benzoglycolic acid is a stronger acid than benzoic acid, the latter is set free, and can now be extracted by means of æther along with some benzoglycolic acid, when pure lime salt is left behind.

When the lime salt dissolved in alcohol is decomposed with sulphuric acid, the acid separates from the filtered solution, on spontaneous evaporation, in tolerably large prisms, which, owing to the predominant expansion of two surfaces, appear as thin tables. The benzoglycolic acid is very sparingly soluble in cold, more readily in hot water, by which it is gradually decomposed. When heated with too little water to dissolve it, it melts into oily drops. It dissolves readily in alcohol and æther. It melts when heated upon platinum foil, and solidifies on cooling into a crystalline mass. At a higher temperature it gives off vapours, which excite coughing, and which contain benzoic acid, and leaves a slight carbonaceous residue, which is readily consumed at a red heat.

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The salts of benzoglycolic acid are for the most part soluble in water, and many of them are soluble in alcohol. From the aqueous solution of most of the salts, the strong acids, even acetic acid, separate the benzoglycolic acid in minute crystals. The analysis of the acid again led to the formula advanced by Strecker—

Carbon.....	60·09	18	= 108	60·00
Hydrogen.....	4·66	8	8	4·44
Oxygen.....	35·25	8	64	35·56

Benzoglycolate of Potash dissolves very readily in water and alcohol, and is very difficult to crystallize.

Benzoglycolate of Soda, NaO, C^{18} H^7 O^7, 6HO, crystallizes more readily than the potash salt, and is obtained, on the cooling of a hot saturated solution, in tolerably large rhombic prisms. It contained 21·0 and 21·08 per cent. water of crystallization. The salt, dried at 212°, furnished—

C^{18} H^7 O^7.....	..	1	= 171·0	84·57
NaO.....	45·42	1	31·2	15·43

Benzoglycolate of Lime, CaO, C^{18} H^7 O^7, HO, is remarkable from its property of forming supersaturated solutions, so that at times perfectly cold solutions, from which even a portion has crystallized, on being passed through a fine cloth strainer, become turbid, and after a few minutes entirely solidify to a thick jelly, owing to the separation of the lime salt. 1 part of the salt dissolves in 7·54 parts water. The salt forms slender silky needles, grouped like wavellite. The crystals are not altered in the air, and do not lose in weight at 212°; they then still contain 1 equiv. water=4·02 per cent., which escapes at 248°. The salt, dried at 212°, furnished—

Carbon.....	52·03	18	= 108	51·92
Hydrogen.....	4·16	8	8	3·85
Oxygen.....	..	8	64	30·77
Lime.....	13·33	1	28	13·46

Benzoglycolate of Baryta, BaO, C^{18} H^7 O^7, 2HO, crystallizes like the lime salt in slender silky needles. It lost 6·67–6·72 per cent. of water at 212°, 2 equivs.=6·78. The salt moreover gave—

C^{18} H^7 O^7 ..	..	..	1	= 171·0	69·06
Baryta.....	30·93	30·90	1	76·6	30·94

Benzoglycolate of Magnesia, prepared by mixing boiling solutions of benzoglycolate of lime and sulphate of magnesia, and exhausting the mass which solidifies on cooling with absolute alcohol, crystallizes on evaporation and cooling in very slender needles.

Benzoglycolate of the Peroxide of Iron, $2Fe^2O^3+3(C^{18}H^7O^7)$, is formed when a solution of benzoglycolate of lime is mixed with perchloride of iron; it is a bulky flesh-red precipitate, which becomes darker at the surface. The salt is completely insoluble in water. The air-dried salt lost at 212°, 27·12 per cent. of water, corresponding to 28 equivs., and gave 23·27 peroxide of iron; the above formula requires 23·32.

Benzoglycolate of Zinc, ZnO, C^{18} H^7 O^7+4HO, obtained by mix-

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ing a boiling solution of the lime salt with chloride of zinc. It forms long, slender, colourless needles, in stellate groups. It lost on desiccation 14·83 and 14·58 per cent. =4 equivs. water, and gave—

$C^{18} H^7 O^7$	..	..	1 =	171·0	80·81
ZnO	19·57	19·27	1	40·6	19·19

Benzoglycolate of Copper, prepared by mixing a boiling solution of the lime salt with nitrate of copper, crystallizes in beautiful blue rhombic prisms; it dissolves very sparingly in cold water, is somewhat more soluble in hot water. When the crystals are heated with less water than sufficient for their complete solution, the undissolved portion forms a green powder, which is probably the anhydrous salt. At 212° the crystals become entirely green and opake.

Benzoglycolate of Lead.—When solutions of the lime salt are precipitated with acetate of lead, the precipitates consist of mixtures of different basic salts. The precipitate from cold solutions is caseous; when heated with water, it first melts, then dissolves completely, and again separates on cooling; the first sediment is amorphous, but after cooling the lead salt separates in crystals. The authors prepared salts of the following composition, the two first by means of neutral acetate, the last with basic acetate of lead:—

1. $3PbO + 2C^{18} H^7 O^7, 3HO$, by spontaneous evaporation of the solution.
2. $PbO, C^{18} H^7 O^7$, obtained from the mother-liquor of the preceding one.
3. $6PbO + C^{18} H^7 O^7 + 2HO$.

Benzoglycolate of Silver, $AgO, C^{18} H^7 O^7$, obtained by precipitating a neutral solution of benzoglycolate of ammonia with nitrate of silver and recrystallization, forms white microscopic crystals, which in the moist state very easily blacken by exposure to the light. It dissolves sparingly in cold, pretty readily in boiling water. The air-dried salt is anhydrous, and lost at 212° only 0·1 per cent. in weight. It gave on analysis—

Carbon	37·76	18 =	108	37·63
Hydrogen.....	2·71	7	7	2·44
Oxygen.....	..	7	56	19·51
Oxide of silver....	40·43	1	116	40·42

In the attempt to prepare the æther of this acid, by treating its alcoholic solution with hydrochloric acid, it was decomposed, and the æther of benzoic acid obtained. However, the composition of the above-described compounds shows that benzoglycolic acid contains 1 atom of water, capable of being replaced by a metallic oxide; consequently its formula is $C^{18} H^7 O^7 + HO$. Its production from hippuric acid by nitrous acid is explained by the equation—

$$C^{18} H^9 NO^6, NO^3 = C^{18} H^8 O^8 + HO + 2N.$$

In its deportment, benzoglycolic acid differs from the other amidogen acids insofar as the derived acid saturates as much base as the hippuric acid, whilst in the other known cases the amidogen acids

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mostly saturate 1 equiv. base less than the liberated acids. Moreover, in this respect hippuric acid is related to aspartic acid, $C^8 H^7 NO^8$, since malic acid, which is derived from it by a similar reaction, saturates just as much base as the aspartic acid. The close coincidence of the per-centage composition of the benzoglycolates and hippurates is also remarkable; for instance, in the lime salts we have—

Benzoglycolate of lime.				Hippurate of lime.			
Carbon.....	18	=108	54·27	Carbon.....	18	=108	54·55
Hydrogen ..	7	7	3·52	Hydrogen....	8	8	4·04
Oxygen	7	56	28·14	Nitrogen	1	14	7·07
Lime	1	28	14·07	Oxygen	5	40	20·20
				Lime	1	28	14·14

The products of decomposition which the authors have obtained from benzoglycolic acid are exceedingly interesting, as they throw further light upon the connexion of hippuric acid with its products of decomposition.

When benzoglycolic acid is boiled for some length of time with a small quantity of dilute sulphuric acid, it is resolved into benzoic acid and a new acid, $C^4 H^4 O^6$, homologous with lactic acid, $C^{18} H^8 O^8 + 2HO = C^{14} H^6 O^4 + C^4 H^4 O^6$.

The new acid, $C^4 H^3 O^5$, HO, the authors call *glycolic acid*, because it agrees with the acid which Laurent and Gerhardt have assumed as the amidogen compound of glycocoll, $C^4 H^4 O^6$, $NH^3 = C^4 H^5 NO^4$, glycocoll + 2HO; but they did not prepare it. They imagined that the acid obtained by Horsford, by the oxidation of glycocoll, $C^3 H^3 O^3$, HO (baryta salt = BaO, $C^3 H^3 O^3$), had been badly analysed, and should be represented by $C^4 H^3 O^5$, HO. However, Horsford's acid is distinct from that of the authors; they have selected this name because their acid does really stand in the relation to glycocoll which Laurent and Gerhardt had imagined of the other.

Glycolic acid is prepared from the baryta salt by decomposing its aqueous solution with dilute sulphuric acid, and filtering and evaporating. The syrupy residue dissolves entirely in æther; the ætherial solution leaves the glycolic acid in the same form on evaporation. It forms a somewhat thick liquid, which mixes in every proportion with water, alcohol or æther. It has a strong acid taste, and gives no precipitate with any metallic salt. It has the greatest resemblance to lactic acid; however, if a solution of glycolic acid is mixed with acetate of lead and an excess of ammonia added, a white flocculent precipitate falls, in which it differs from lactic acid, which under similar circumstances furnishes no precipitate.

Glycolate of Baryta, BaO, $C^4 H^3 O^5$, is obtained when the liquid which remains after the treatment of benzoglycolic acid with sulphuric acid, and crystallizing out the benzoic acid, is saturated with carbonate of baryta, separated from sulphate of baryta, and set aside to crystallize. The salt separates from a syrupy solution; it melts when heated into a perfectly clear liquid, which on cooling again solidifies to a crystalline mass. When further heated, it puffs up

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considerably, diffusing a peculiar odour, and leaves a carbonate of baryta, which is of a somewhat grayish colour, but which quickly burns white. The analysis of the air-dried salt gave—

Carbon	16·82	4	= 24·0	16·71
Hydrogen	2·27	3	3·0	2·09
Oxygen	..	5	40·0	27·86
Baryta	52·70	1	76·6	53·34

Glycolate of Zinc, $ZnO, C^4 H^3 O^5, 2HO$, is obtained by saturating a boiling solution of glycolic acid with an excess of carbonate of zinc; on cooling, crystalline crusts separate, which have the greatest resemblance to lactate of zinc. The individual crystals are minute, colourless, transparent prisms, in stellate groups. The zinc salt is insoluble in alcohol, sparingly soluble in cold, more readily in hot water; 100 parts contain 2·94 parts of anhydrous glycolate of zinc, or 1 part zinc salt dissolves in 33 parts of water. The air-dried salt lost at 212°, 14·64 and 14·37 per cent. of water. The salt, dried at 212°, furnished on analysis—

Carbon	22·69	4	= 24·0	22·33
Hydrogen	3·00	3	3·0	2·79
Oxygen	..	5	40·0	37·21
Oxide of zinc	37·64	1	40·5	37·67

Glycolate of Silver, prepared by decomposing glycolate of baryta with sulphate of silver, was decomposed in the solution, and deposited black flakes. On evaporating the solution over sulphuric acid *in vacuo*, a gradual blackening likewise took place, and the residual tenacious residue no longer dissolved completely in water. The same want of success attended the attempt to precipitate the glycolate of silver from its aqueous solution by an addition of alcohol; æther likewise caused no turbidness.

Glycolic Acid, $C^4 H^4 O^6$, neutralizes 1 equiv. base, and not 2, as Laurent and Gerhardt assume according to their theory. Were glycolic acid a bibasic acid, its formula should be written $2HO, C^8 H^6 O^{10}$. The analysis of the glycolate of zinc shows that it contains 2 equivs. water of crystallization, corresponding to the paralactate of zinc (lactic acid from the fluids of the flesh). If lactic acid is regarded as a conjugate compound of formic acid with the aldehyde of acetic acid, glycolic acid would appear to be a corresponding compound with the aldehyde of formic acid:—

$C^6 H^6 O^6$, lactic acid $= C^2 H^2 O^4$, formic acid $+ C^4 H^4 O^2$, aldehyde.
$C^4 H^4 O^6$, glycolic acid $= C^2 H^2 O^4$, formic acid $+ C^2 H^2 O^2$, formylaldehyde.

Glycolic acid is also produced by the action of nitrous acid upon glycocoll. Glycocoll is decomposed, even in its aqueous solution, by nitrous acid, with disengagement of nitrogen. If the solution be now evaporated, the glycolic acid is converted into oxalic acid. If, on the other hand, the solution of glycocoll, treated with nitrous acid, is shaken with æther, the glycolic acid is dissolved out,

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and left on evaporation as a syrupy liquid. This production of glycolic acid from glycocoll is—

$C^4 H^5 NO^4$, glycocoll + $NO^3 = C^4 H^4 O^6$, glycolic acid + HO + 2N.

It comes therefore to the same thing whether benzoglycolic acid is first prepared from hippuric acid by nitrous acid, and this then decomposed by ebullition with acids, or the hippuric acid is first resolved into benzoic acid and glycocoll, and the latter then treated with nitrous acid.

It is highly probable that benzoglycolic acid may be prepared from benzoic acid and glycolic acid, since the authors have succeeded in preparing artificially the homologous benzo-lactic acid.

A mixture of lactic and benzoic acids, heated to 356° F. as long as any liberation of aqueous vapour was perceptible, solidified on cooling into a resinous mass, which was dissolved in water with the addition of potash. To the hot solution, dilute sulphuric acid was added as long as on cooling a crystallization of benzoic acid was observed, and until the crystals which separated exhibited a different form. The acid which now separated was collected on a filter, and the filtrate mixed with cold dilute sulphuric acid. A copious precipitate formed, which on ebullition with water first melted, dissolved in much water, and on cooling separated partly in drops and partly in crystals. This acid was dissolved in æther, and again obtained in crystals by evaporation; it was neutralized with ammonia, and precipitated with a solution of silver. The precipitate was analysed, and furnished 39·7 per cent. of silver; the formula AgO, $C^{20} H^9 O^7$ requires 38·5 per cent. of oxide of silver.

The formation of this new acid, which the authors call benzolactic acid, is readily explained by the following equation:—

$C^{14} H^6 O^4$, benzoic acid + $C^6 H^6 O^6$, lactic acid = $C^{20} H^{10} O^8$, benzolactic acid + 2HO.

Ann. der Chem. und Pharm., lxxx. p. 17.

On the Action of Nitric Acid upon Citraconic Acid. By S. Baup.

A short time ago, Gottlieb* described a new acid under the name of mesaconic acid, which he obtained by treating citraconic acid with dilute nitric acid; it is isomeric with itaconic and lipic acids.

Baup, who has been engaged in a similar investigation, observed that citraconic acid, mixed with a liquid consisting of 4 parts water and 1 part nitric acid, furnishes an acid isomeric with citraconic acid; but that strong nitric acid, which acts very powerfully upon the acid, forms, among other products, an oily liquid, which is separable into two substances.

The author observes, that at the time Gottlieb published his researches, his own were not concluded. His communication refers consequently partly to the statements of Gottlieb, and partly to new

* Chem. Gaz., vol. ix. p. 233.

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facts not noticed by that chemist. Pebal's * paper on the salts of mesaconic acid does not seem to have been known to the author.

Mesaconic Acid.—Baup has proposed the name *citracartic acid*, compounded of *citraconic* and *ars*, for this acid; and endeavours to justify this change of name. However, to avoid useless synonyms, we retain Gottlieb's denomination, which is more euphonious.

According to Baup, mesaconic acid dissolves in 38 parts of water at 57° F., in 29 parts of water at 72°, in 2·6 parts of alcohol of 0·838 spec. grav. at 72°. It is also soluble in æther, from which it crystallizes in flat prisms. It sublimes previous to melting, burns with a blue flame without any residue of carbon; it gives white precipitates with basic acetate of lead and protonitrate of mercury, and a brown flaky one with perchloride of iron; neutral acetate of lead furnishes with it a crystalline salt. The solution of a mesaconate is precipitated by salts of silver, copper, and by perchloride of mercury. The following statements of Baup should be compared with Pebal's:—

Mesaconate of Potash.—The neutral salt is deliquescent; the acid salt crystallizes in micaceous laminæ, is readily soluble in water, and sparingly soluble in alcohol.

Mesaconate of Soda.—The neutral salt is not crystallizable; the acid salt is obtained in rhombic prisms, which are not altered in the air.

Mesaconate of Ammonia.—The neutral salt does not crystallize; the acid salt separates in small prisms with three terminal facettes, soluble in 8 parts of water. According to the author, its composition is represented by NH^3, $C^{10} H^4 O^6$, 2HO; found atomic weight =146·3 and 145.

Mesaconate of Baryta, 2BaO, $C^{10} H^4 O^6$ + 8HO. Prismatic, transparent, four-sided prisms, frequently flat or tabular, undergoing no alteration in the air, except that they effloresce in dry air, but again absorb the lost water in a humid atmosphere. The salt puffed up very considerably on being heated, lost on desiccation 21·07 water, and furnished 45·39 per cent. baryta. The above formula requires 21·35 and 45·44.

Acid Mesaconate of Baryta, BaO, $C^{10} H^4 O^6$, 2HO, small prisms, unalterable in the air, furnished 36·64 per cent. baryta; the above formula requires 37·07.

Neutral Mesaconate of Lime, 2CaO, $C^{10} H^4 O^6$, 2HO, minute acicular crystals forming by their union white fibrous masses, which dissolve in 16·5 parts of water at 68°; insoluble in alcohol. At a slightly elevated temperature it parts with its water of crystallization, and absorbs it again on exposure to the air; it puffs up less than the baryta salt on ignition, and furnished 30·00 per cent. of lime; theory requires 30·11.

Neutral Mesaconate of Lead.—The neutral lead salt is obtained by precipitating a neutral mesaconate with acetate of lead; the precipitate is at first caseous, but becomes crystalline. From very dilute solutions it separates in small, short, transparent, flattened

* Chem. Gaz. vol. ix. p. 281.

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prisms. The anhydrous salt contains 66·63 per cent. oxide of lead. It contains water of crystallization.

Acid Mesaconate of Lead, $PbO, HO\ C^{10} H^4 O^8$, is deposited from the solution of the free acid when this is mixed with acetate of lead. It forms prismatic crystals, which puff up when heated, which is not the case with the neutral salt. It furnished 47·90 oxide of lead; the formula requires 48·07.

Basic Mesaconate of Lead, $4PbO, C^{10} H^4 O^9, 6HO$, is precipitated from a solution of the neutral salt by the addition of tribasic acetate of lead; the precipitate is first flocculent, and then pulverulent. The salt loses about 6 per cent. of water in drying previous to its turning yellow. It contained 72·35 per cent. of oxide of lead.

Neutral Mesaconate of Copper, $2CuO, C^{10} H^4 O^6, 4HO$, is obtained by mixing solutions of mesaconic acid and acetate of copper in minute, granular, dark blue crystals. It furnished 35·03–34·80 per cent. of oxide of copper; the above formula requires 35·9.

If a neutral mesaconate be decomposed by acetate or sulphate of copper, besides the above salt there is found another basic one, which is of a greenish-gray colour.

The above statements relate to the salts of mesaconic acid. In conclusion, it should be observed that Baup considers mesaconic acid, or his citracartic acid, as monobasic, and has therefore taken the acid salts as binacid. As an example, we will take the two baryta salts above described; the neutral salt is $BaO, C^5 H^2 O^3, 4HO$, and the acid salt is $BaO, 2C^5 H^2 O^4, 2HO$. The atomic weight of the acid is 56.

Eulyte, Dyslyte.—It has already been stated, that citraconic acid, on treatment with concentrated nitric acid, furnishes an oily substance, which is converted on cooling into a yellow mass, diffusing on ebullition with water an aromatic odour, resembling that of mint, and imparting a sweet taste to the water.

After standing for some time with water, the substance became crystalline. Hot alcohol of 0·838 resolved it into two substances of different solubility.

Eulyte, which is the most soluble substance, crystallizes from alcohol in white striated prisms of a silky lustre; from its solution in æther it separates in transparent shining crystals; alcohol of 0·838 spec. grav. dissolves it very readily with the assistance of heat; water at 50° F. dissolves only $\frac{1}{10,000}$dth. The substance melts under hot water; if on cooling it should remain liquid, it suffices to touch it with a sharp body to cause it to solidify. After being melted, it solidifies into a laminar mass, which however no longer takes place when it has been long exposed to heat. At a higher temperature it is entirely volatilized, and diffuses the odour of amyrine. Heated in a closed tube, it gives off red fumes, which burn with a flame when set light to; hot concentrated sulphuric acid dissolves it, but the greater portion crystallizes out on cooling.

Dyslyte.—This substance, which is least soluble in alcohol, crystallizes from the solution in transparent, shining, small, four-sided prisms, which are very fragile. From æther it separates in acicular

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crystals. At 50°, 1 part requires 2200 parts of alcohol of 0·838, and 15,000 parts of alcohol of 0·807 for solution. It is nearly insoluble in water, 1 part requiring about 24,000 parts at 50° F.; it does not melt in water, but in hot water appears to become partially crystalline. When melted, it solidifies on cooling into prismatic crystals, even when it has been kept for some time in a state of fusion. The substance is volatilized at a higher temperature in acicular crystals, diffusing the odour of mint or cummin. It dissolves in concentrated sulphuric acid.—Liebig's *Annalen*, Jan. 1852, p. 192.

Researches on Populine.

By M. PIRIA, *in a Letter to* M. Dumas.

You are aware that in 1830 M. Braconnot announced the discovery of a crystalline substance, which he had succeeded in extracting from the leaves and bark of the aspen (*Populus tremula*), and which he called populine. A recent investigation of this substance has led me to the following results:—

After having unsuccessfully attempted to resolve populine by means of synaptase, I had recourse to other agents; and the reactions which I observed have led me to regard this substance as a complex group, resulting from the union of benzoic acid, saligenine, and grape-sugar into one molecule. The products of decomposition by the action of various reagents are precisely the same as those which would result from the metamorphosis of the secondary groups which it contains. Thus with a mixture of bichromate of potash and sulphuric acid, populine yields hydruret of salicyle very abundantly; on ebullition with concentrated nitric acid, it is converted into nitrobenzoic acid, trinitrated phenic acid and oxalic acid; lastly, under the influence of acids, it is decomposed into benzoic acid, saliretine and grape-sugar.

The elementary constitution of populine is represented by the formula $C^{40}H^{22}O^{16}+4Aq$. At 212° it parts with its 4 equivs. water, and becomes perfectly anhydrous. This formula results from the union of equal equivalents of benzoic acid, saligenine and sugar, with elimination of 4 equivs. water, as seen by the following equation:—

$$C^{14}H^{6}O^{4}+C^{14}H^{8}O^{4}+C^{12}H^{12}O^{12}-4HO=C^{40}H^{22}O^{16}.$$

We might also regard populine as the result of the union of a molecule of benzoic acid with a molecule of salicine less 2 equivs. of water; we should then have—

$$C^{26}H^{18}O^{14}+C^{14}H^{6}O^{4}-2HO=C^{42}H^{22}O^{16}.$$

This mode of viewing its molecular constitution having led me to foresee the possibility of converting populine into salicine, I made some experiments in this direction, by which my suppositions have been realized with unexpected success. It is merely requisite to boil some populine with barytic water to obtain in a few minutes a perfectly limpid and colourless solution, which, after separation of the excess of baryta by a current of carbonic acid, contains nothing

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further than benzoate of baryta and salicine. The salicine thus prepared is decomposed, under the influence of synaptase and acids, like ordinary salicine, and behaves absolutely in the same manner towards other reagents. Two analyses of the artificial salicine gave the following numbers:—

Carbon	54·20	54·65
Hydrogen	6·36	6·41

which are identical with those which had been obtained by the analyses of ordinary salicine.

If populine be dissolved in the cold in 10–12 times its weight of pure nitric acid of 1·30 spec. grav., it produces a new substance, which I call benzohelicine. Benzohelicine is not decomposed by synaptase; but under the influence of acids and alkalies, it is resolved into hydruret of salicyle, benzoic acid and grape-sugar. Consequently this substance stands in the same relation to helicine as populine to salicine; and it will perhaps be advisable to substitute the term benzosalicine for the word populine. Benzohelicine is converted into helicine when boiled with caustic magnesia, which removes from it the benzoic acid it contains, without altering the helicine.

Before concluding this letter, allow me to communicate another fact, which may prove interesting to some chemists; it is the existence of the homologue of acetone in the æthalic series. Æthalone is obtained with the greatest facility by distilling æthalic acid quickly with an excess of slaked lime. In order to purify it, it is crystallized several times from boiling alcohol; it separates in thin nacreous plates, which have the following composition:—

Carbon	82·46	82·94	62 =	372	82·67
Hydrogen	13·94	14·04	62	62	13·78
Oxygen	..	..	2	16	3·55

Comptes Rendus, Jan. 26, 1852.

Observations on Tungstic Acid. *By* J. Persoz.

When crude tungstic acid, as procured from wolfram, is treated with 5 or 6 times its weight of nitre, taking the precaution to operate at gradually-elevated temperatures, three different salts are obtained, which have distinct characters, and contain acids, which cannot be confounded one with the other.

If the mixture is exposed to a temperature scarcely higher than that of the fusing-point of the nitre, only a portion of the crude tungstic acid is attacked, and the bubbles of nitrous vapours cease to be disengaged as soon as this first action is accomplished, provided the temperature remains stationary. On treating with hot water the product of this first fusion, we obtain a salt A in solution and an insoluble residue x.

On treating this residue x with a large excess of nitre, and exposing it to a temperature not much lower than that at which the

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nitre is decomposed, a fresh portion of the crude tungstic acid is attacked, and the mass, from being pasty, becomes very fluid, but not transparent. When this saline mass is exhausted with boiling water, the excess of nitre and a large quantity of a salt, which we shall call B, is removed; after these washings there remains a residue insoluble in water as long as it is charged with nitre, but which immediately passes through the filter on being washed with pure water. This insoluble residue we shall call salt C.

We will now proceed to examine the products thus separated.

Salt A.—The solution of A, left to itself, deposits the free nitre, if any be present, and then on cooling congeals to a crystalline mass, which, according to the temperature and the degree of purity of the salt, presents the apparent characters of boracic acid or those of the chlorate of potash. What is most remarkable is, that these crystals are essentially composed of nitre, water, and a few thousandths of a salt of the tungstic group. When submitted to the action of boiling water, they are decomposed, and there is obtained a solution of pure nitre and a flocculent deposit, which, after numerous washings with concentrated hydrochloric acid, forms a mealy powder, insoluble in those acids which have great affinity for water, and very soluble in water.

The solution, evaporated to dryness to expel the hydrochloric acid, leaves a yellowish-white residue, which redissolves entirely in pure water, and furnishes a solution which possesses acid properties in the highest degree.

This acid A strongly reddens blue tincture of litmus; its solution does not precipitate the nitrate of silver; it is reduced by zinc, and passes into the state of an inferior oxide of the purest blue colour; lastly, on treatment with acids which have great affinity for water, this acid in solution parts with its hydrate water, and immediately regenerates the mealy powder above mentioned. Under the air-pump the solution of the acid A is soon converted into a yellow crystalline mass, like sulphur crystallized by fusion, or of a milk-white colour, assuming the form of regular octahedra when the acid is purest.

Salt B.—The solution of this salt is composed of an excess of nitre and of tungstate of potash properly so called, from which may be prepared tungstic acid and its salts, which are easily obtained pure and of definite composition, when they invariably furnish a yellow precipitate with the protochloride of tin.

Insoluble Salt C.—This salt, heated to redness with twice its weight of caustic potash, and the fused mass treated with water, furnishes an insoluble residue of peroxide of iron and a liquid, which, on the addition of a slight excess of nitric acid, yields on ebullition a milky-white pulverulent precipitate, which is a distinct acid from the preceding ones. Both in the free state and in all the combinations we have examined, this acid C cannot be treated with pure water without passing through the filter. In other respects it possesses most of the characters of tungstic acid, and like it is soluble in ammonia and the other caustic alkalies; it is attacked by the

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bisulphate of potash, and is precipitated from its solutions by certain acids, reduced by hydrogen, passing into the state of blue oxide, gray oxide or metal. It differs however from tungstic acid by such distinct and permanent characters, that it is impossible to confound the two. Thus, for instance, its colour passes, under the influence of heat, from white to yellow, returning to its primitive state on cooling. It is insoluble in hydrochloric acid under circumstances in which tungstic acid is readily soluble; and, on the contrary, dissolves in nitric acid, whilst tungstic acid under the same circumstances is perfectly insoluble in it. It appears to approximate to niobic acid in other properties, but differs by several important characters, which we shall describe when we have compared experimentally the two acids.

The three salts we have isolated appear well-defined and distinct, but when mixed they react one on the other so much as to cause important modifications in their respective properties; and these modifications vary according to the proportion in which they are mixed. This explains all the contradictory particularities in the history of the tungstates.—*Comptes Rendus*, Jan. 26, 1852.

On the Atomic Weight of Tungsten, and on some of its Compounds. By J. B. VON BORCH.

The author has determined the atomic weight of tungsten by oxidizing the metal into acid, and also by the reduction of the acid to metal. He finds for it the number 1150 taking O=100, consequently 92 with H=1. The results given below agree with those of Schneider*, and may be looked upon as confirming the researches of that chemist. The column A contains the per-centage amount of metal which the acid contains, B the corresponding atomic weight:—

					A.	B.
By reduction:—						
I.	6·1942	grms. of acid give	4·9132	metal	79·310	1150·60
II.	5·7744	...	4·5740	...	79·212	1143·14
III.	8·4353	...	6·6883	...	79·289	1148·51
IV.	7·1520	...	5·6725	...	79·313	1150·19
V.	7·0304	...	5·5698	...	79·225	1144·05
VI.	3·9854	...	3·1600	...	79·290	1148·57
VII.	2·7636	...	2·1916	...	79·302	1149·42
By oxidation:—						
VIII.	3·1505	grms. of metal gave	3·9700	acid	79·359	1153·42
IX.	1·6550	...	2·0860	...	79·339	1152·01
			Mean.....		79·294	1148·85

Tungstate of Ammonia and Peroxide of Iron, $Fe^2O^3, 5NH^3, 10WO^3, 13HO$.—When wolfram from Schlackenwalde, $(FeO, WO^3)^2 + (MnO\,WO^3)^3$, is dissolved in hydrochloric acid, and the dried tungstic acid dissolved in ammonia, there separates, on evaporating

* Chem. Gaz., vol. viii. p. 401.

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the ammoniacal salt, an oily substance, which dries into a resinous mass, and is then translucent and has a vitreous fracture. It is insoluble in cold water and alcohol, but soluble in hot water. It consists of—

Peroxide of iron	5·5	1 =	5·5
Tungstic acid.....	80·8	10	80·5
Ammonia	4·5	5	5·8
Water	9·2	13	8·2

When the above compound has been removed, nearly pure acid tungstate of ammonia crystallizes out, which can be obtained pure and perfectly free from iron by further crystallization. When the mother-liquor from the acid tungstate of ammonia is further evaporated, it can be concentrated to the thickness of a syrup, and dries into a dark gummy mass, which on resolution furnishes on slow evaporation octahedral crystals mixed with chloride of ammonium. The octahedra are of a brown colour, have an exceedingly bitter taste, and dissolve in every proportion in hot and cold water. Their per-centage composition was found to be 84·4 tungstic acid, 4·6 oxide of iron and manganese, 4·0 ammonia, and 7·0 water. Some undecomposed mineral, silica, gangue, and a brick-coloured powder, which contains ammonia, iron, manganese and tungstic acid, remain on the filter.

Pure tungstic acid is obtained, according to the method of Buchholtz, by fusing the mineral with carbonate of potash, exhausting the mass with boiling water with the addition of some alcohol, precipitating the alkaline liquid with chloride of calcium, and decomposing the tungstate of lime with hydrochloric acid. The acid obtained in this manner furnishes with ammonia a salt, which contains no iron or manganese.

Sulphuret of Tungsten, WS^2, is obtained pure, according to Berzelius's method, by heating to redness a mixture of pure tungstic acid with vermilion, or metallic tungsten with sulphur. The dry nut-brown sulphuret of tungsten, which forms on the addition of hydrochloric acid to a solution of tungstic acid in sulphuret of ammonium, and the brownish-black which is produced by the addition of hydrochloric acid to a solution of tungstate of ammonia after decomposition by sulphuretted hydrogen, always contain tungstic acid and a tolerable amount of water.

Bromide of Tungsten, WBr^2.—Metallic tungsten is heated in a current of dry bromine gas free from air. A deep yellowish-red gas is formed, which is deposited in the form of an opake black crust. By sublimation in a current of carbonic acid, it is obtained in the form of a woolly mass of acicular crystals, which readily melt on being heated, and are converted on ebullition into a yellowish-red mass. They are decomposed by water into pseudo-amorphous crystals of whitish-yellow or yellow tungstic acid and hydrobromic acid. On analysis they furnished—

Tungsten	37·47	1	36·53
Bromine	62·13	2	63·47

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On passing bromine over tungsten, a less volatile product is obtained, which after repeated sublimation forms a black compound inclining to violet or blue. It boils, and sublimes close to its melting-point; and its gas, compared with that of WBr^2, is almost purple-red, and so dark that it appears black even in very thin layers. On cooling, it condenses into a compact mass with crystalline texture; but it also separates in long, very large, and shining quadratic prisms, which are truncated. Heated with access of air, the compound absorbs oxygen, and $WBr^3 + 2WO^3$ sublimes. It constantly gives off fumes of hydrobromic acid in the air, and is converted into blue oxide. It dissolves in caustic alkalies with evolution of hydrogen, and is decomposed by water, without any evolution of heat or gas, into blue tungstic oxide and hydrobromic acid. Its per-centage composition was found to be—

Tungsten ..	32·76	31·03	31·95	31·95	31·92	5	31·53
Bromine ..	66·94	68·70	67·71	65·96	67·33	2	68·47

Biaciperbromide of Tungsten, $WBr^3, 2WO^3$.—This compound is very easily procured by passing bromine gas over blue tungstic oxide, or over sulphuret of tungsten, or over a mixture of tungstic acid and charcoal; it is usually obtained in yellow scales, but on slow sublimation in quadratic prisms or scales. It has a different colour according to the mode of preparation; it is of a beautiful brick-red when prepared from the sulphuret, lemon-coloured from the oxide, and brassy or grayish from the mixture of tungstic acid and charcoal. It volatilizes without melting, but is less volatile than the preceding compound. In the air and in water it is converted into hydrobromic and tungstic acids. It furnished on analysis—

Tungsten	49·18	49·73	49·75	48·68	3	48·96
Bromine.....	40·66	41·69	41·20	..	3	42·53
Oxygen.....	10·16	8·58	9·08	..	6	8·51

The author could not obtain the two *oxybromides* $WBr^5 + W^2O^5$ and $2WBr^2 + WO^3$, the *oxychloride* WCl^3, WO^3, nor the *protochloride* WCl, which are said to exist by Bonnet.

Chloride of Tungsten, WCl^2, is obtained by heating tungsten, or, what is preferable, the sulphuret of tungsten, in a current of chlorine; it melts, forms a reddish-yellow gas, and then solidifies into a woolly crystalline mass. It decomposes very readily in the air into yellow tungstic acid. In water it changes into white tungstic acid, which subsequently turns yellow, with disengagement of hydrogen. It gave on analysis—

Tungsten	56·77	56·87	56·79	57·55	1	56·48
Chlorine.....	43·23	43·13	33·21	42·46	2	43·52

Perchloride of Tungsten, W^2Cl^5 or $WCl^3 + WCl^2$, which was first made known by Malaguti, is contained in the brownish-red sublimate which is formed on heating metallic tungsten in chlorine. When this sublimate is again sublimed in chlorine, it forms a dark brownish-red brittle mass, with a crystalline fracture, which melts

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on the application of heat, then boils, and is converted into a reddish-yellow gas, resembling that of nitrous acid. On slow crystallization, the compound is obtained in large brownish-red, translucent, and shining quadratic prisms, with truncated angles. When heated in the air, they decompose into WCl^2 and WCl^3+2WO^3. In water and with access of air, they are resolved into hydrochloric acid and blue oxide, which gradually passes into tungstic acid. They dissolve in caustic alkalies with disengagement of hydrogen; but the solution becomes turbid on the application of heat, and deposits brown tungstic oxide. The following numbers were obtained on analysis:—

Tungsten	51·37	50·70	61·85	50·97	2	50·95
Chlorine	48·21	48·28	48·15	47·12	5	49·05

Biacichloride of Tungsten, WCl^3+2WO^3, which was first made known by H. Rose and Malaguti, and is obtained when chlorine is passed over oxide of tungsten, or a mixture of tungstic acid and charcoal, and is formed in general when chlorine is passed over tungsten with access of air, is white inclining to grayish-yellow, and crystallizes in scales; it volatilizes without previously melting, but is decomposed when the temperature is raised rapidly into WO^3 and WCl^2, which latter is volatilized along with free chlorine. Analysis gave—

Tungsten	64·01	3	64·14
Chlorine	24·17	3	24·72
Oxygen.....	11·82	6	11·14

Journ. für Prakt. Chem., vol. liv. p. 254.

On some new Compounds of Cobalt. *By* M. Rogojski.

M. Claudet has published, in the Philosophical Magazine for October 1851, a paper on some new ammoniacal compounds of cobalt, in which, among other things, he points to the existence of a protochloride of a most extraordinary composition, and without example in the known series of compounds.

At the desire of M. Gerhardt, I have undertaken in his laboratory some experiments on the same subject, with the view to throw some light on the composition of this singular body, and to obtain some new facts which would serve to explain its true nature.

In the course of this investigation I have discovered a new compound entirely different from that of M. Claudet, which promises to throw some light upon the problem which I seek to solve. It is a chloride analogous to the ammoniacal chlorides discovered by M. Reiset, or rather to the ammoniacal chlorides of the same metal discovered more recently by M. Gerhardt, and corresponding to the platinic salts. In fact, my new chloride belongs to the per-, and not to the ordinary protosalts of cobalt. It crystallizes in small orange prisms, which are extremely soluble in water, whilst M. Claudet's salt is obtained in small crimson octahedra, and are nearly insoluble in that liquid.

According to several analyses, the new chloride contains CO^2Cl^3,

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$3N^2H^6$, a formula, which may be rendered by ClH, N^2H^5 co, giving to co the value of $\frac{2}{3}$Co.

In fact, it is a hydrochlorate, which furnishes by double decomposition the corresponding sulphate, nitrate, acetate, &c. A characteristic reaction of this chloride is obtained with the bichloride of platinum. When solutions of the two salts are mixed together, there is formed in the cold a yellow precipitate, which would be taken for the ammonio-chloride of platinum, but which is distinguished from that salt by its dissolving in hot water, and crystallizing on cooling in small prisms. This precipitate is the platinochloride of the base contained in my new chloride. It contains $PtCl^2$, ClH, N^2H^5 co.

This base, to which I give the name of *dicobaltinamine*, represents a double molecule of ammonia, in which 1 atom of hydrogen is replaced by its equivalent of *cobalticum*. It is perfectly analogous to the bases obtained with platinum by M. Gerhardt and Reiset, as will be seen by the following table:—

N^2H^5Pt, diplatosamine.	NH^2Pt, platosamine.
$N^2H^4Pt^2$, diplatinamine.	$NHPt^2$, platinamine.
N^2H^5 co, dicobaltinamine.	NH^2 co, cobaltinamine (unknown).

I may observe, in conclusion, that my new base is not indicated in the two short notes recently published by M. Fremy.—*Comptes Rendus*, Feb. 2, 1851.

ANALYTICAL CHEMISTRY.

Indirect Method of determining Magnesia and Alkalies conjointly. *By* Dr. K. List.

In order to avoid the tedious operations which are required for an actual separation of magnesia, potash and soda, especially when they do not exist together in the state of pure chlorides, I have endeavoured to determine them conjointly by an indirect method. In the following paper I shall describe the process which I have hitherto found practically applicable in the most complicated case, such as is presented by the analysis of a silicate decomposed by hydrofluoric acid.

The filtrate obtained after precipitation of all other bases is evaporated to dryness in a water-bath. and the residue of sulphates and chloride of ammonium cautiously ignited in a platinum crucible, to drive off the ammoniacal salts. All loss may be prevented in this operation by employing a crucible lid with an interior convex surface. As it is an indispensable condition for the success of the determination that there should be no other acid present but sulphuric, the ignited saline mass is moistened with a little dilute sulphuric acid, and again evaporated to dryness. To convert the acid salts into neutral, a piece of carbonate of ammonia is then placed in the crucible, and this again heated until the bottom becomes feebly red.

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This operation is repeated until the weight remains constant*. The contents of the crucible are now dissolved in water, and the sulphuric acid in the solution determined by chloride of barium; after the excess of baryta has been removed by sulphuric acid, the magnesia is precipitated by ammonia and phosphate of soda, and determined in the usual manner.

From these three data—

The quantity of sulphates ..... $=A$†
The quantity of sulphuric acid contained in them .. $=S$
The quantity of magnesia contained in them ..... $=m$,

the quantity of potash and soda is calculated. If by S′ is represented the sulphuric acid combined with m (which, when the quantity of magnesia is small, may be taken as $2m$), and by s the sulphuric acid combined with potash and soda, by a the quantity of alkaline sulphates contained in A, then—

$$a=A-(m+S') \text{ and } s=S-S'.$$

If, further, the atomic weights of potash, soda, and sulphuric acid are respectively represented by KO, NaO and SO^3, the quantity of potash (k) and soda (n) contained in the mixture is found by the formula—

$$k=\frac{\frac{s.NaO}{SO^3}+s-a}{\frac{NaO}{KO}-1} \text{ and } n=\frac{\frac{s.KO}{SO^3}+s-a}{\frac{KO}{NaO}-1};$$

or

$$k=\frac{1{\cdot}77829\,.\,s-a}{-0{\cdot}33816} \text{ and } n=\frac{2{\cdot}17595\,.\,s-a}{0{\cdot}5109}.$$

I have proved the applicability of this method upon a known mixture of sulphates of potash, soda and magnesia. After having convinced myself of the purity of the individual salts by a determination of their sulphuric acid, 0·1805 KO, SO^3, 0·0725 anhydrous NaO, SO^3, and 0·0605 anhydrous MgO, SO^3, were mixed and treated in the manner described. I obtained 0·4762 BaO, SO^3 and 0·0591 $2MgO, PO^5$; consequently the mixture contained—

	Mixed.	Found.	Difference.
Potash.....	0·09765	0·09877	+0·0011
Soda	0·03176	0·02999	−0·0017
Magnesia.....	0·02039	0·02162	+0·0012

The sources of error by which the minute difference is caused are, at all events, of much less importance in this method than in that of direct separation, especially as the determinations of sulphuric acid and magnesia are among those operations which can be effected with the greatest accuracy.—Liebig's *Annalen*, Jan. 1852.

* A direct experiment convinced me that in this operation the pure MgO, SO^3 loses no sulphuric acid.

† If the whole is not dissolved when treated with water, the insoluble residue must be deducted from A. If the method described is accurately followed, this insoluble part will, at the utmost, amount to only a few milligrammes, and will consist of the remains of previously imperfectly-separated substances.

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CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Application of Organic Chemistry to Perfumery.

From a Letter written by Dr. HOFMANN *to* Prof. Liebig.

THE beautiful investigations of M. Cahours upon the oil of *Gaultheria procumbens*, which have made us acquainted with the nature of this compound, so much used in perfumery, appears not to have been lost sight of in the arts.

The arrangement of the oil of winter-green in the group of the compound æthers could not do otherwise than direct the attention of the manufacturers of perfumery to this extensive class of bodies, the number of which is still further daily increased by the active energy devoted to the field of organic chemistry. The remarkable fruity odour of many of these æthers had not been overlooked by chemists; but it was reserved for practical men to make the selection and ascertain the proportions in which certain of these compounds resembled in so great a degree the aroma of particular fruits, that we almost feel ourselves led to the idea, that these very compounds are the cause of the odour of the fruits in question, and that they would be found in them, if the processes were followed on a sufficiently large scale.

The artificial production of aromatic oils for commercial purposes has only been carried on for the last few years; but although the process of fabrication is so new, yet it appears to be already in the hands of several distillers, some of whom make tolerably large quantities. The jury were enabled to satisfy themselves of this, in their examination of the products belonging to this department in the Exhibition. We found in our surveys at the Exhibition, both in the English and in the foreign divisions, a copious selection of these chemical articles of perfumery, the applicability of which was moreover illustrated by the simultaneous exposition of the confectionary flavoured with them.

Unfortunately, most of these oils were only sent in small quantities, so that the specimens which I was enabled to obtain, in few cases only allowed of accurate examination.

The compound most frequently exhibited was a liquid labelled "*pear oil*," which on examination was shown to be an alcoholic solution of pure *acetate of amylic oxide*. As I had not enough of the compound to allow of its sufficient purification for ultimate analysis, I decomposed it with potash, when free fusel oil separated, and the acetic acid was determined in the form of the silver salt. The acetate of silver gave per cent.—

Theory.	Experiment.
64·68	64·55

The acetate of amylic oxide, when obtained by the ordinary process (1 part of sulphuric acid, 1 part of fusel oil, and 2 parts of acetate of potash), evolved a remarkably fruity odour; but the agreeable odour of the Jargonelle pear was not distinct until it was diluted with 6 vols. of alcohol. On close inquiry of the exhibitors, I ascertained that tolerably large quantities of this oil (in one case 15–20 lbs.

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weekly) are manufactured. It is principally used for flavouring pear-drops, which are much admired in England, and which consist almost entirely of barley-sugar.

Next came the *apple oil.* As the examination shows, it is nothing more than valerianate of amylic oxide, and every one is at once reminded of the insupportable odour of rotten apples, which fills the laboratory, in making valerianic acid. When the crude distillate of this operation is treated with dilute alkali, the valerianic acid is separated, and an æther is obtained, the solution of which in about 5 or 6 vols. of alcohol possesses a most agreeable aroma of apples.

The essence in greatest quantity was the *pine-apple oil*, which, as you are aware, is only butyrate of oxide of æthyle. This compound, also, like the two above, does not evolve the agreeable odour until diluted with a large amount of alcohol. Butyric æther, which in Germany is frequently added to the inferior kinds of rum, is principally used here for flavouring a kind of lemonade (pine-apple ale). For this purpose it is however seldom prepared from pure butyric acid, but generally by merely saponifying the butter, and distilling the soap with concentrated sulphuric acid and alcohol. The liquid thus obtained of course contains other æthers besides butyric æther, but it may be used in this state for flavouring. The specimen which I analysed appeared however to be the pure æther prepared from butyric acid. When decomposed by potash and converted into a silver salt, it yielded—

Experiment.	Theory.
55·33	55·38 per cent. of silver.

The so-called *cognac oil* and *grape oil* were sent both by English, as also French and German exhibitors. They appear to be used pretty commonly for imparting the favourite cognac odour to low brandies. Unfortunately the specimens exhibited were too small in quantity to allow of my instituting an accurate examination of these oils. The cognac oil especially was in very small quantity; on the addition of water to the whole of the sample, a few drops only separated, and these consisted of a mixture. The grape oil is also an amyle compound, dissolved in much alcohol; for when treated with concentrated sulphuric acid, the oil, freed from alcohol by washing with water, yielded sulphate of amylic oxide, which was identified by the analysis of the barytic salt. It yielded 45·82 per cent. of sulphate of baryta.

The crystallized amylo-sulphate of baryta with 2 equivs. of water, analysed by Cahours, and again recently by Kekulé, contains 45·95 per cent. of sulphate of baryta. It is certainly remarkable, that we see here a body, which on account of its insupportable odour is separated from brandy with the greatest care, again applied in an altered form to flavour this beverage.

I must also allude to the *artificial oil of bitter almonds.* When Mitscherlich, in 1834, discovered nitrobenzole, he little thought, after twenty years, to find this body in an industrial exhibition. He certainly, at that time, pointed out the remarkable resemblance which the odour of nitrobenzole had to that of oil of bitter almonds: but the only sources for obtaining benzole at that time, viz. the oil

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of compressed gas and the distillation of benzoic acid, were much too expensive, and put an end to the idea of substituting the use of nitrobenzole for oil of bitter almonds. However, as you recollect, by means of the well-known aniline reaction, I showed with the utmost certainty the presence of benzole in the common light oils of coal tar, which had frequently been previously suspected; and in 1849, C. B. Mansfield showed, by a careful investigation, that benzole may be procured easily, and in large quantity, from oil of coal tar. In his memoir, which contains many valuable details upon the practical applications of benzole, the possibility that the fragrant nitrobenzole may be obtained in larger quantities is alluded to. As the Exhibition shows, this remark has not been lost sight of in the arts. Among the articles of French perfumery, with the title of *artificial oil of bitter almonds*, and the fanciful name of *essence of Mirbane*, there were several specimens of oils, which on accurate examination proved to consist of more or less pure nitrobenzole. I was not enabled to ascertain accurately the extent of this fabrication; but it appears to me by no means inconsiderable. Here, in London especially, tolerable quantities of this artificial oil of bitter almonds are prepared. The very simple apparatus used is that proposed by Mr. Mansfield. It consists of a large glass worm, the upper end of which branches into two tubes, which are provided with funnels. A stream of concentrated nitric acid flows slowly through one of these funnels, whilst the other is for the benzole (which for this purpose need not be absolutely pure). At the point at which the tubes of the funnels are united, the two bodies come in contact; the chemical compound formed becomes sufficiently cooled in passing through the worm, and only requires to be washed with water, and finally with some weak solution of carbonate of soda, to be ready for use. Although the nitro-benzole closely resembles oil of bitter almonds in physical properties, it possesses however a somewhat different odour, readily recognised by a practised hand. However, it answers well for scenting soap, and would be extensively applicable for confectionary and for culinary purposes. For the latter purpose it has the special advantage over oil of bitter almonds, that it contains no prussic acid.

Besides these, several other similar products were exhibited, but most of them were of too compound a nature, and in too small a quantity, to allow of their composition being accurately determined. In the case of many of these essences, their resemblance to the aromas specified was very doubtful.

The application of organic chemistry to perfumery is still in its infancy; and we may expect that a careful survey of those æthers and ætherial compounds with which we are at present acquainted, and those which are daily being discovered, will lead to further results. The interesting caprylic æthers, which M. Bouis has lately discovered, are remarkable from their extremely aromatic odour; (thus the acetate of caprylic oxide possesses an odour as strong as it is agreeable), and promise, if they can be obtained in larger quantities, to yield new materials for perfumery.—*Ann. der Chem. und Pharm.*, vol. lxxxi. p. 87.

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THE CHEMICAL GAZETTE.

No. CCXXVI.—March 15, 1852.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Chemical Examination of crude Wood-Spirit.
By Dr. C. Vœlckel.

According to the investigations of Liebig, Gmelin, Schweitzer and Weidmann, the so-called crude wood-spirit consists of several substances. The true wood-spirit, the hydrate of the oxide of methyle of this mixture, is the constituent which readily forms a crystalline compound with chloride of calcium, from which the other substances can be in some measure separated by distillation. Gmelin called that portion which did not combine with chloride of calcium, or only with difficulty, lignone. Schweitzer and Weidmann distinguish in it xylite and mesite.

From the author's investigations, it appears that wood-spirit contains a large number of volatile substances, which resemble each other in composition, and do not differ very much in their deportment. These substances are products of decomposition of acetic acid, as proved by their composition. They have been formed by the elimination of water and carbonic acid from the elements of acetic acid, $C^4 H^3 O^3 + HO$, at a high temperature. The remaining member, $C^3 H^3 O$, has assumed a different state of density according to the temperature at which the decomposition occurred; and in this manner these similar substances have been formed.

Vœlckel examined the crude wood-spirit from Kaltmann's manufactory at Solothurn; it was a colourless liquid, but soon became yellow by exposure to the air. It was first distilled alone, then mixed with chloride of calcium, which dissolved in it with evolution of heat, and on cooling solidified to a crystalline mass, from which a small portion of a volatile fluid was distilled off in the water-bath. This distillate was again left for some time over a large quantity of chloride of calcium, then distilled, and in order to remove every trace of the hydrate of oxide of methyle (the compound of chloride of calcium with wood-spirit always giving off some wood-spirit at 212°), left for several days with fresh chloride of calcium, decanted and distilled alone. The clear colourless liquid begins to boil at 131° F.; perfect ebullition occurs at 140°; the thermometer then rises slowly to 144°, where it remains stationary for some time, and now rises slowly to 149°, 158°, 176°, 194°, 212°, and at last to 248°,

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at which temperature the distillation was discontinued, there being but little liquid left in the retort.

It is evident, from the rising of the boiling-point, that the liquid consists of a mixture of several substances.

Vœlckel collected the portion A, which passed over between 131° and 160°, apart, and likewise that which distilled over between 160° and 248°. The first portion has the same properties as the xylite of Schweitzer and Weidmann; but according to Vœlckel it is not a simple body, but a mixture of three, viz. *acetate of the oxide of methyle*, *acetone*, and a liquid which has the same composition as acetone, and to which Vœlckel has appropriated the name of *xylite*.

Liquid A.—The mixture which passed over between 131° and 160° cannot, according to Vœlckel, be separated into the above-mentioned constituents by further treatment with chloride of calcium; nor was it possible, according to the method described by Schweitzer in Löwig's Chemistry, to distil the crystals of chloride of calcium and xylite, which are produced when the liquid is mixed with fused chloride of calcium. Vœlckel effected the separation by fractionated distillation. The four fractions had the following boiling-points and composition:—

	Boiling-point at 131°–140°.	140°–145°.	145°–150°.	150°–160°.
Carbon	58·36	58·63	60·82	61·91
Hydrogen.....	10·02	10·17	10·46	10·43
Oxygen	31·62	31·20	28·72	27·66

The first of these fractions contains the acetate of methyle and acetone, which is mixed with a trace of xylite (Vœlckel's). If the liquids which pass over between 131° and 150° are distilled with hydrate of lime, a portion is decomposed into acetic acid, which is held combined with the lime, and hydrate of oxide of methyle, which distils over with the undecomposed portion. When this distillation had been repeated till no further change—no further production of acetate of lime—occurred, the undecomposed liquid which had passed over was distilled first with a small quantity of chloride of calcium, to remove the greater portion of the water and wood-spirit; and then, in order to get rid of every trace, left for some time in contact with several pieces of chloride of calcium, poured off, and distilled alone on the water-bath.

The liquid decanted from the chloride of calcium possesses a somewhat different odour from that of the original liquid; it is more penetrating and ætherial, and is allied to that of acetone. It mixes in every proportion with water, alcohol and æther, and is again separated from the aqueous solution by solid chloride of calcium. It burns with a bright, highly-luminous, non-fuliginous flame. When heated in the distillatory apparatus, it begins to boil at 131°, but the boiling-point soon rises to 140° and 142°; that which passed over at 142° was collected apart; it amounted to about the fifth part of the liquid used for distillation. From 142° the boiling-point slowly rises to 144°, at which temperature it remains for a short time stationary, and then rises slowly to 145°; between

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142° and 145° about a third of the liquid passes over; about the same quantity between 145° and 149°, from which temperature the boiling-point slowly rises to 151°. Some chloride of calcium, which had been dissolved in the liquid, is left in the retort. The specific gravity of the first portion is 0·803, of the second 0·805, and of the third 0·809. The analyses of all these three products agree with each other and with the composition of acetone pretty accurately :—

Carbon.....	60·53	60·81	60·95	3	=225·00	62·07
Hydrogen ..	10·44	10·60	10·58	3	37·50	10·34
Oxygen	29·03	28·59	28·47	1	100·00	27·59

The above analyses do not accurately agree with the composition of acetone; but if the substance be previously purified by leaving it for some length of time in a vessel half-filled with milk of lime, then distilled off, dehydrated by chloride of calcium, distilled, and only that portion which passes over between 136° and 140° collected, the specific gravity is 0·802, and it furnishes on analysis :—

	I.	II.			
Carbon.....	61·90	61·66	3	= 225·00	62·07
Hydrogen.....	10·45	10·43	3	37·50	10·34
Oxygen.....	27·65	27·91	1	100·00	27·59

The liquids which pass over between 142° and 145°, between 145° and 150°, and also between 150° and 160°, have all the same composition :—

	I. 142°–145°.	II. 145°–150°.	III. 150°–160°.
Carbon	61·90	61·87	61·91
Hydrogen	10·54	10·48	10·43
Oxygen	27·56	27·65	27·66

Consequently all these liquids, I., II., III., which distil over between 131° and 160°, have the composition of acetone; they are however not acetone, but a mixture of acetone with xylite (Vœlckel's), which has the same composition. Between 131° and 140° a mixture of acetone with xylite passes over, and between 142° and 160° the same mixture, with another substance of still higher boiling-point, which could not be further examined.

The acetone contained in crude wood-spirit amounts to so little, that, in order to obtain it, it is necessary to operate upon large quantities. Not quite an ounce of a liquid which passed over between 131° and 142°, and of which about one-half was acetone, was obtained from 24 litres.

The *Xylite* of Vœlckel, $C^{12}H^{12}O^4$, boiled between 142° and 143°. It is a clear, colourless, very mobile liquid, of a peculiar penetrating odour, pungent taste, and specific gravity 0·805. It mixes in every proportion with water, alcohol and æther; it is again separated from the aqueous solution by chloride of calcium, and also by alkali. Xylite burns with a very luminous, non-fuliginous flame. Pure xylite does not combine with finely-pulverized potash; it does not immediately experience the slightest change, and only after some time turns brown, owing to its partial conversion into resin. The formation of the crystalline salt, observed by Schweitzer and Weidmann,

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is owing to the presence of the acetate of methyle. The crystalline salt is the double salt of acetate of potash and acetate of methyle with wood-spirit and potash. If this salt be dissolved in water, the wood-spirit potash is decomposed; the liberated potash then decomposes on boiling the acetate of methyle into wood-spirit and acetate of potash.

Whilst xylite is scarcely decomposed by potash when the action is but of short duration, there is formed, according to the experiments of Schweitzer and Weidmann, with which the authors agree, the following substances,—xyliten-aphtha, xyliteole and xylite-resin, when the amount of potash is considerable and the reaction is continued for some time. These substances have, according to Schweitzer and Weidmann, the following composition:—

Xylite-naphtha ..... $=C^{12}H^{12}O^{3}$
Xyliteole..... $=C^{12}H^{9}O$
Xylite-resin..... $=C^{8}H^{6}O$

According to the author, xylite-naphtha has the formula $C^{12}H^{11}O^{3}$, and it is that portion of the product of decomposition of xylite by the action of potash which passes over between 230° and 248°. This xylite-naphtha is lighter than water, and has a somewhat different odour from xylite; it is identical with that portion of the liquid B which distils over between 230° and 248°. It gave on analysis—

Carbon.....	66·95	12 =	900·00	67·28
Hydrogen	10·67	11	137·50	10·28
Oxygen	22·33	3	300·00	22·44

The author prefers the formula deduced from this analysis to that of Schweitzer and Weidmann, because it explains better the formation of xylite-naphtha from xylite, since—

$$C^{12}H^{12}O^{4}-HO=C^{12}H^{11}O^{3}.$$

The xylite-naphtha is then converted, by the long-continued action of potash, into xyliteole, as follows:—

$$C^{12}H^{11}O^{3}-2HO=C^{12}H^{9}O.$$

Lastly, with respect to the formation of xylite-resin, this can have originated only by hydrogen and oxygen having separated in the proportion in which they form water from the composition of xylite. Xylite changes far more readily into resin in the presence of potash when the air has free access than otherwise; 2 atoms xylite absorb 1 atom oxygen from the atmosphere, and give 1 atom xylite-resin and 6 atoms water—

$$C^{24}H^{24}O^{8}+O=C^{24}H^{18}O^{3}+6HO.$$

Xylite and Sulphuric Acid.—From the dark brown mixture of equal parts by weight of xylite and sulphuric acid, water separates only a little coloured resin. About half the xylite can be obtained unaltered from this acid liquid by distillation in the water-bath. By further distillation over a fire, xylite-naphtha and xyliteole are obtained. Another portion of the xylite has been converted by the concentrated sulphuric acid into a brown resin, which separates on neutralizing the liquid. A very small quantity of a conjugate sul-

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phuric acid is formed in this operation; for when a portion of the acid liquid, which was not distilled in the water-bath, was saturated with carbonate of lead, the liquid filtered from the sulphate of lead contained but a trace of lead in solution, and on evaporating it at a gentle heat, a very small quantity of a soft substance was left. The resinous mass which is formed in this operation is, according to Schweitzer and Weidmann, a brown substance, and is identical with the resin produced by the action of potash upon xylite. The author has not examined this resin more closely.

When crude xylite, by which is understood the liquid passing over between 140° and 158°, and having the formula $n(C^3 H^3 O)$, is distilled with an equal weight of concentrated sulphuric acid, undecomposed substance first passes over; subsequently, with evolution of a large amount of sulphurous acid, a yellowish oily liquid, methole, which floats on the surface of an aqueous liquid; whilst the residue consists of a resinous substance, which is carbonized with considerable tumescence on the continued application of heat. The distillate was mixed with an excess of caustic potash, and the xylite, which had passed over undecomposed, removed by distillation in the water-bath. When at 212°, nothing further passed over; the distillation was continued over a fire so long as methole distilled over with the water.

Methole is a clear colourless liquid, lighter than water, of a peculiar odour, which is totally different from that of xylite. The liquid, dehydrated over chloride of calcium, begins to boil at a little above 212°, but only a few drops of oil pass over, whilst the thermometer gradually rises to 320°; from 320° it distils over more rapidly, the boiling-point constantly rising until at last it has reached 428°, at which temperature the distillation was discontinued, as the retort only contained a little thick slightly-yellowish liquid. According to this, methole is by no means a simple substance. The portion which passed over between 338° and 356° gave on analysis—

	Voelckel.	Schweitzer and Weidmann.			
Carbon.....	83·17	81·81	82·90	87·92	86·72
Hydrogen ..	10·52	10·23	10·47	10·87	11·28
Oxygen	6·31	7·96	6·63	1·21	2·00

Schweitzer and Weidmann deduced from their analyses the formula $C^4 H^3$ or $C^{12} H^9$:—

Carbon	88·88	4 =	300·00
Hydrogen	11·12	3	37·50

Since, judging from the analysis and the boiling-point, the methole which passed over between 338°–356° appeared to be a mixture of volatile substances, some containing oxygen, others none, the whole of the methole was treated with concentrated sulphuric acid. After long standing, a clear colourless liquid had separated on the dark brown-coloured sulphuric acid; the clear liquid was removed, and again treated with half its volume of fresh concentrated sulphuric acid. After separation of the sulphuric acid, the liquid was washed with water, rectified with water, and dehydrated

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over chloride of calcium. This methole has the following properties:—It is a clear colourless fluid, of a peculiar odour, lighter than water, in which it is insoluble, but soluble in alcohol and æther. It is not acted upon immediately by concentrated nitric or sulphuric acid, but after a long time it is decomposed by these acids. It burns with a very luminous smoky flame. It begins to boil at 320°, but perfect ebullition does not take place before 338°, from which temperature the thermometer constantly ascends until it finally reaches 428°, the liquid distilling over all the time. The distillate was collected in two portions; the first portion boiled between 320°–374°, and its specific gravity was 0·868; the second boiled between 374°–428°, and its specific gravity was 0·879; they furnished on analysis—

Carbon	89·66	89·74	3 =	225·00	90·00
Hydrogen.....	10·33	10·27	2	25·00	10·00

This methole is consequently a mixture of substances of the formula $n \cdot C^3 H^2$. These hydrocarbons are identical with those which the author prepared from the volatile oils of wood-tar by treatment with concentrated sulphuric acid.

Liquid B, *with boiling-point between* 158°–248°.—This liquid was again submitted to a fractionated distillation; at first a liquid passed over between 144°–160°, which was identical with that already described under A; the five following fractions are characterized by their boiling-points; that which passed over between 158°–167° corresponds to the mesite of Schweitzer and Weidmann. Contrary to the statements of those chemists, it is soluble in every proportion in water, and burns with a luminous, non-fuliginous flame. The liquid which passed over between 167°–176°, as also that collected between 176° and 194°, does not differ in composition from xylite so much as to prevent our assuming that these liquids likewise consist of bodies isomeric with acetone and xylite.

The liquids which distilled over between 167°–194° float upon a small quantity of water, and require a very considerable amount for their solution, the more the higher their boiling-point. They burn, like the following, with a very luminous, non-fuliginous flame. Those fluids which were collected between 194°–212° and between 212°–248°, consist undoubtedly for the greater part of products of decomposition of acetone, xylite, &c. by heat. This applies especially to those liquids which pass over between 212° and 248°, which are identical with xylite-naphtha, which is produced by the action of caustic potash and sulphuric acid upon xylite. The effect of heat therefore upon xylite is like that of potash and sulphuric acid; all three agents effect a separation of hydrogen and oxygen in the form of water. Analysis gave—

Boiling-point...	158°–167°.	167°–176°.	176°–194°.	194°–212°.	212°–248°.
Spec. grav.....	=0·813.	0·818.	0·820.	0·828.	0·835.
Carbon.....	62·18	63·35	63·68	65·64	66·95
Hydrogen ..	10·66	10·74	10·76	10·84	10·67
Oxygen	27·16	25·91	25·56	23·52	22·38

Poggendorff's *Annalen*, lxxxiii. pp. 272, 557; and lxxxiv. p. 101.

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On a new Salt of Iridium. *By* C. KARMRODT *and* E. UHRLAUB.

In working up some platinum residue according to the usual method, by heating it with chloride of sodium and chlorine, we accidentally obtained a new salt of iridium, which, from its forming large regular crystals, deserved to be more closely examined.

This salt is a combination of the sesquichloride of iridium with chloride of sodium and water of crystallization, $Ir^2 Cl^3 + 4NaCl + 27HO$; it forms very large, dark brown, almost opake crystals, the fundamental form of which is a klinorhombic octahedron. These crystals soon begin to effloresce in the air, and become liquid at 122° F. Over sulphuric acid they fall to a grayish-brown loose powder. This salt requires half its weight of water for solution; the solution has a beautiful brownish-red colour, but it cannot again be crystallized from it; it only crystallizes from a saturated solution of chloride of sodium.

It is obtained when the platinum residue, mixed with salt, is heated to incipient redness in chlorine, the mass exhausted with water, the filtered dark brownish-red solution concentrated by evaporation, and then set aside for several days.

The salt lost over sulphuric acid 24·5 per cent., or 21 atoms of water. When heated gradually to 392° F., it lost in several experiments 31·1 per cent., or 27 atoms; consequently the whole amount of water. For further analysis, 0·8375 grm. of the anhydrous salt was heated to redness in a bulb-tube in hydrogen gas, and the hydrochloric acid formed condensed in a bulb-apparatus containing water; it furnished 0·717 chloride of silver =0·177 chlorine, calculated for the hydrated salt; the tube lost 0·179. From the mixture of iridium and chloride of sodium the latter was extracted with water, and precipitated by a solution of silver; it furnished 0·876 chloride of silver, corresponding to 0·358 of sodium. The iridium, dried at 392°, weighed 0·297; on further examination it proved to contain one-half per cent. of osmium and a trace of iron. A second analysis was made in the same manner. The following are the results:—

	I.	II.	Calculated.
Iridium	24·43	24·60	25·24
Chlorine	14·56	14·63	13·62
Chloride of sodium	29·59	29·57	30·03
Water	31·10	31·10	31·11
	99·68	99·90	100·00

A third analysis was made by precipitating a solution of the salt with nitrate of silver, which caused a very bulky greenish-brown precipitate, from which only that portion of chloride of silver could be extracted by ammonia, which had been furnished by the chloride of sodium. The dark greenish-brown portion of the precipitate insoluble in ammonia, proved on analysis to be a definite compound of sesquichloride of iridium with chloride of silver, $Ir^2 Cl^3 + 3AgCl$:—

	Found.	Calculated.
$Ir^2 Cl^3$	40·97	41·36
AgCl	59·06	58·64

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It was analysed by heating it to redness in hydrogen, and subsequent extraction of the silver with nitric acid. The portion of iridium which was not precipitated by the silver salt was, after separating the excess of silver with hydrochloric acid and evaporation, determined by igniting the saline mass in hydrogen.—Liebig's *Annalen*, Jan. 1852.

On the Extract of Gentian. By Dr. Mohr.

The gentian root is ground fine in a mill, 12 lbs. of water poured over it, in which it is allowed to swell, and brought into an earthen sugar-cone stopped at the bottom with straw. The liquid which runs off has a dark colour, but is perfectly clear; the last portions of liquid are poured upon fresh substance. The exhausted root has still a somewhat bitter taste; but it does not yield, on ebullition with water, any deeper-coloured solution than the last bright extract. The solution prepared by boiling, is, on the contrary, turbid, and remains so; nor could it be clarified. On boiling the exhausted root with caustic potash or carbonate of soda, and then adding an excess of acid, thick flakes of pectic acid separated, which, after being purified by decantation and dried, formed coloured masses, which behaved precisely like pectic acid. The cold extract gave, on the addition of acid, no precipitate; it contained therefore no pectine.

The liquids were evaporated on the water-bath with constant stirring. Before they had acquired the consistence of an extract, they became thick and turbid, and an insoluble substance separated from the clear liquid. If the evaporation is continued, a large quantity of extract is obtained, which dissolves to a very turbid solution. To ascertain the nature of the substance which caused the turbidity, a portion of the extract was largely diluted, poured upon a filter, and the sediment well washed. It formed a swollen smeary mass. Diffused in water, it no longer dissolved on ebullition, nor on being boiled with sulphuric acid. It dissolved readily and entirely in a boiling solution of caustic potash, carbonate of soda and ammonia. Peracetate of iron produced no alteration of colour; it contained therefore no tannine. A solution of iodine in iodide of potassium likewise produced no alteration, showing the absence of starch. After being dried and heated upon platinum, it did not melt, but gave off vapours and was charred. The cinder was easily burnt to ash, which had an alkaline reaction, and consisted of carbonate of potash and carbonate of lime. The entire amount of ash was small.

The author concludes from these experiments, that this substance forms a weak acid, which has probably been produced during the evaporation by the influence of the air. It was precipitated by acids from its alkaline solution and decomposed carbonate of soda when warmed with it with effervescence, yielding a clear liquid. This substance, after being washed, possessed no remarkable bitterness, and did not diffuse the odour of gentian when charred; it was therefore not a necessary ingredient of the extract. The author recom-

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mends that this substance, the nature of which could not be ascertained more precisely, should be removed from the extract, for which purpose the latter is diluted with water and passed through a coarse paper filter. Linen strainers, &c. soon become stopped up, and do not answer so well as paper filters, although the operation proceeds very slowly with these. The author obtained from 12 lbs. of root 4 lbs. of extract. The author strongly recommends treatment with cold water.—*Archiv der Pharm.*, lxviii. p. 145.

On the Existence of Copper in the Blood of the Limulus.
By Dr. F. A. Genth.

It is known that the *Limulus* found on the coasts of North America has blue blood. Its colour is frequently very light, but sometimes also a dark sky-blue. The author found it always to contain a tolerably considerable proportion of copper, together with a very slight quantity of iron. Neither metals can be detected in the ordinary manner by means of reagents, but with the greatest ease and certainty when the blood is boiled for some time with an excess of caustic potash. By this means the albumen is dissolved, and a part of its sulphur combines with the metals. After filtering and combustion, the precipitate is dissolved in nitric acid, and phosphate of lime and oxide of iron precipitated by ammonia. The filtrate has a cærulean-blue colour, gives with sulphuretted hydrogen a blackish-brown precipitate, and after the addition of hydrochloric acid and ferridcyanide of potassium a purple-red. The iron was detected in the solution of the phosphate of lime in hydrochloric acid by means of sulphocyanide of potassium.

The blood is very easily obtained by making an incision in the back between the two shells of the animal. It flows immediately in large quantity, from large specimens even as much as a pound. For the first moment it has a whitish-blue or sky-blue, but muddy colour. After a few seconds, fibrine separates, but the blue colour of the liquid remains, and does not disappear until after a long time, frequently several days. On boiling the blue solution, it coagulates immediately, albumen separates, and with it the copper, in consequence of which the solution becomes clear like water. It has the smell of boiled sea-fish. In order to obtain the ash, the blood was evaporated to dryness in a spacious dish, and heated to complete carbonization. So as not to lose any chlorides in the subsequent complete combustion, the author preferred extracting the carbonized mass with water, by which means the residue was rendered easy of combustion, and evaporated the solution to dryness after the completely burnt ash of the residue had been mixed with it. The dry mass was then thoroughly rubbed together, feebly ignited, and submitted to analysis.

1. The blood of two female individuals, taken before the laying of the eggs at the end of May. Animals very lively before tapping; colour deep sky-blue. The analysis of the ash gave the following results:—

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	per cent.
Chloride of sodium	79·207
Chloride of potassium	4·607
Chloride of magnesium	3·848
Sulphate of potash	3·264
Sulphate of lime	2·159
Carbonate of lime	2·950
Phosphate of magnesia	1·709
Magnesia	1·959
Oxide of iron	trace
Oxide of copper	0·295
	100·000

2. Blood of a male, taken in July, animal not lively, from Cape Henlopen. Colour whitish-blue. Specific gravity at 77° F.=1·0317. The blood contained 3·327 per cent. fixed constituents, 3·088 per cent. soluble in water, and 0·239 per cent. insoluble in water; the ash contained 92·814 per cent. of soluble parts and 7·186 per cent. insoluble. The composition of the ash is the following:—

	per cent.
Chloride of sodium	83·507
Chloride of potassium	2·395
Chloride of magnesium	1·840
Sulphate of potash	1·686
Sulphate of magnesia	3·470
Carbonate of lime	1·448
Pyrophosphate of magnesia	0·444
Magnesia	5·128
Oxide of iron	0·081
Oxide of copper	0·085
	100·084

It appears that the variation in the composition of the blood of the *Limulus* is partially determined by the consumption of certain constituents at the time of fecundation and laying the eggs, which are again gradually replaced as soon as this act is completed; possibly it is also dependent upon the locality and the composition of the water in which these animals live. In any case, the difference, especially in the quantity of copper, is so considerable, that it admits of very interesting chemico-physiological questions, as to the functions which the copper fulfills in the vital œconomy of these animals.—Keller and Tiedemann's *Nordam. Monatsber.*, vol. iii. pp. 294 and 438–441.

Examination of Bread to determine the per-centage of Bran. *By* MM. Wetzel *and* Van Hees.

The authors endeavoured to determine by experiment—

1. How much bran was contained in corn upon an average.
2. How much bran the seven-pound loaf ought to contain legally.

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3. How a fraudulent addition of wheat- or rye-bran might be detected.

They found, in the first place, that by exhausting rye with water at 212° F., 3 oz. of rye left 193 grs. of insoluble residue as the mean of seven experiments. It is therefore admissible to consider in round numbers the quantity of bran in 3 oz. of rye-grain as 200 grs.

They then determined how much soluble matter the ordinary bran of wheat and rye contained respectively, in order to be able from these data to calculate how much ordinary bran the bread ought to contain. Various samples of commercial wheat-bran were treated in the same way as the rye-grains, and gave as a mean that 100 grains of wheat-bran left 50 grs. of insoluble residue. 288 grs. of commercial rye-bran left upon the average 107 grs. of insoluble dry substance.

According to the previous determinations, it follows that 3 oz. of rye-grain ought to contain $1\frac{1}{13}$ oz. of ordinary bran.

In cases where bread has been adulterated with bran, it is very easily distinguishable whether the bran used was that of wheat or rye. The wheat-bran assumes a bright yellow colour after extraction with water, while that of rye appears much darker; the former also appears very smooth and thin, while the latter is more tenacious and shrivelled.

In the examination of bread containing an addition of bran, the authors boil a weighed quantity of bread in the same way as the rye, and weigh the insoluble residue. From this the amount of bran is calculated.—*Archiv der Pharm.*, lxvii. p. 284.

On the Decomposition of Carbonic Acid by Twigs of Viscum album. *By* Dr. E. Luck.

Several physiologists having expressed the opinion that parasitic plants derive their nutriment exclusively from the juices of the plants on which they grow, the author exposed some twigs of *Viscum album* to the light of the sun in water containing carbonic acid. It is important to observe that the leaves of this plant are not green, but greenish-yellow. Experiment showed that 2 oz. of twigs had disengaged in the course of two hours 20 cub. centims. of gas, which consisted of—

Oxygen	61·5
Carbonic acid	8·8
Nitrogen	29·7

Ann. der Chem. und Pharm., lxxviii. p. 85.

On Oxide of Chromium crystallized in the Dry Way, and on the Arseniate of the Protoxide of Cobalt. By M. Gentele.

Oxide of Chromium.—When bichromate of potash is exposed for eighteen hours, in a porcelain crucible, to the temperature of the porcelain furnace, the crucible will subsequently be found to con-

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tain fine spangles of oxide of chromium, which exhibit a play of many colours.

Arseniate of the Protoxide of Cobalt, $4CoO, AsO^5$.—The monobasic arseniate of the protoxide of cobalt is now frequently manufactured on a large scale by adding a solution of carbonate of potash to a solution of arseniate of protoxide of cobalt in nitric acid, which contains peroxide of iron. At first, basic arseniate of the peroxide of iron falls; but on filtration, after the whole of the iron has been precipitated, or when carbonate of potash is added as long as the precipitate is white, and then filtered, a rose-red precipitate is obtained on the further addition of carbonate of potash, which consists of hydrated basic arseniate of the protoxide of cobalt, and is known in commerce by the name of *chaux métallique*. This salt appears to be a mixture of two compounds, in different atomic portions, and with a different amount of water. The author exposed this technical product to the temperature of a porcelain furnace, and found that it fused to a perfectly crystalline mass, the cavities of which were filled with beautiful bright rhombic prisms. They are of a deep dark blue colour, furnish a rose-coloured powder, and dissolve readily in acids. Analysis furnished—

Protoxide of cobalt	55·90	4	56·58
Arsenic acid	42·50	1	43·42
Porcelain mass of the crucible	1·60		

This compound, to judge from the analysis, has originated from the *chaux métallique* by the volatilization of arsenic.—*Journ. für Prakt. Chem.*, vol. liv. p. 185.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Manufacture of Oxalic Acid.

Oxalic acid is formed by the action of nitric acid on a great number of vegetable substances, such as sugar, rice, starch, washed sawdust, &c.

Sugar, either in its crystalline state or in that of molasses or treacle, is the substance more commonly employed in the manufacture of oxalic acid.

On the addition of nitric acid to the saccharine solution and exposure to heat, a substitution of part of the oxygen of the nitric acid for the hydrogen of the sugar is effected, oxalic acid being formed and deutoxide of nitrogen evolved from the liquor. Other changes than this however take place; carbonic acid is often disengaged with the deutoxide of nitrogen, and saccharic acid and other products remain in solution with the oxalic acid.

Instead of cane-sugar or treacle, the saccharine substance formed by the action of sulphuric acid on potato or other starch (as in Mr.

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Nyren's process) is employed. For this purpose the potatoes are well washed, and then reduced into a fine pulp by rasping, grinding, or other suitable means; such pulp is then washed two or three times by placing it in water and well stirring it therein, then permitting the pulp to subside, and running off the water. The pulp thus obtained is next placed in an open vessel of lead, or wood lined with lead, with as much water as will allow of the mixture being boiled freely by means of steam passed through leaden pipes placed therein. Into the mixture of pulp and water about 2 per cent. by weight (of the potatoes employed) of sulphuric acid is to be stirred in, which will be at the rate of from 8 to 10 per cent. of acid on the quantity of farina contained in the potatoes; the whole is now to be boiled for some hours until the pulp of the potatoes is converted into saccharine matter; the completion of this process being readily ascertained by applying a drop of tincture of iodine to a small quantity of boiling liquor placed on the surface of a piece of glass, when, if there be any farina remaining unconverted, a purple colour will be produced. The saccharine product thus obtained is then filtered through a horse-hair cloth, after which it is carefully evaporated in any convenient vessel until a gallon of it weighs about 14 or 14½ lbs. It is now in a proper condition to be employed in the manufacture of oxalic acid, by the application of nitric acid, as in the case of operating upon sugar or treacle. Horse-chestnuts, deprived of their outer shells, are also applicable to the manufacture of oxalic acid when treated in the way above described for potatoes.

Instead of operating with sulphuric acid, the farina of potatoes and of chestnuts may be treated with diastase, and converted into a liquor similar to that obtained after evaporation from the farina and sulphuric acid before mentioned, using about the same proportion of diastase as above directed for sulphuric acid. In this case the liquor is made of the required strength at once, and the processes of filtration and evaporation are rendered unnecessary.

The apparatus required in the conversion of the saccharine matter (whether of cane-sugar or formed of starch in the way above mentioned) into oxalic acid is very simple. Usually, earthenware jars of about two gallons capacity are employed, which, when charged with nitric acid and the saccharine material used, are placed in water-baths capable of holding a hundred or more of these jars. These baths are constructed of brick and lined with lead, and are heated by means of steam passed through coils of lead pipe placed therein.

Instead of earthenware jars, vessels of lead, or of wood lined with lead, may be employed in the manufacture of oxalic acid. For this purpose, square open vessels, 8 feet square and 3 feet deep, are a convenient size, the liquor being heated by means of steam passed through a coil of lead pipe. A coil of about 48 feet of one-inch pipe, in a vessel of the size above mentioned, is sufficient to keep the liquor at the required temperature. In using these vessels, the liquor (whatever it may be) to be converted into oxalic acid is put into them, together with the acid employed, and heated until the

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required decomposition is effected. The liquor is then drawn off by a syphon, or by a cock placed at the bottom of the vessel, into shallow leaden vessels, or wooden vessels lined with lead, to cool and crystallize, and the mother-waters are drawn off from the crystals and used in the next operation.

When the manufacture of this acid is conducted in large vessels as above mentioned, the specific gravity of the nitric acid employed may be less than when the earthenware jars are used. From 1·200 to 1·270 are about the limits of the range allowed for the gravity of the acid. As regards the temperature of the baths, this should be maintained at or about 125° F. Whilst the operation is in progress, the active evolution of gas, without the appearance of red fumes, and the emission of a peculiar smell, slightly indicative of the presence of nitric oxide, are amongst the signs that everything is in good working condition. The judicious addition of sulphuric acid is found to contribute to an increase of the quantity of oxalic acid produced. The product of acid from a given quantity of sugar has been much understated by chemical writers; this has most probably arisen from the circumstance of boiling the sugar with strong nitric acid, by which means a large quantity of oxalic acid becomes converted, as soon as formed, into carbonic acid; and the result is, that the actual product of oxalic acid obtained represents only about one-half of the sugar employed, and therefore not above one-half the quantity which should have been obtained. Thus we find it stated, that from 50 to 60 lbs. of oxalic acid are obtainable from 100 lbs. of good sugar, whereas the quantity actually obtained in practice is from 125 to 130 lbs. Treacle of course gives a smaller product, 100 lbs. of fair quality yielding from 105 to 110 lbs. of oxalic acid.

The mother-liquor having been poured off, the crystals of acid obtained are thrown on drainers and washed, and then carefully dried in a suitable stove. The mother-liquors, when treated with a fresh supply of nitric acid and treacle, are ready for a further operation.

About $4\frac{3}{4}$ cwts. of nitrate of soda and $2\frac{1}{2}$ cwts. of sulphuric acid are used to furnish the nitric acid required to convert 1 cwt. of good sugar into oxalic acid.

Mr. Jullion has patented a process for the conversion of formic acid into oxalic acid. For this purpose, formic acid is saturated with a solution of caustic potash, and then half the quantity of caustic potash required for saturation is added to the above mixture; the whole is then evaporated to dryness, and heated to 560° F. By this process, the formic acid is decomposed, and oxalate of potash formed. Caustic soda may also be employed instead of caustic potash.

The oxalate of potash or of soda thus obtained is then treated with sulphuret of barium, hydrate of baryta, or any soluble salt of baryta, whereby an oxalate of baryta is precipitated, from whence pure oxalic acid may be obtained by means of sulphuric acid.

Another mode of obtaining oxalic acid is by the process patented by Dr. Wilton Turner, who directs the uric acid obtained from

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guano to be treated with peroxide of lead or manganese suspended in water, at a boiling temperature, by which means it will be decomposed into oxalic acid, allantoin and urea. The oxalic acid forms an insoluble compound with the lead or manganese. The lead process is as follows:—A known weight of uric acid is placed in an open cylindrical iron vessel, capable of holding 2 lbs. of water for every pound of the acid, and adapted to boil by steam. A clear saturated solution of lime-water is then added, and as soon as it is heated and in brisk ebullition, the peroxide of lead is added in successive portions as long as it is observed to be whitened by the boiling liquid. The whitish powder thus obtained is oxalate of lead. About 240 lbs. of peroxide of lead are required for each 168 lbs. of uric acid employed. The supernatant liquor is next drawn off, and the oxalate of lead washed with clear water; this is then boiled with dilute muriatic acid (equal parts of acid and water), by means of which oxalic acid is obtained in solution, which is evaporated and crystallized, whilst muriate of lead remains as the precipitate.

The allantoin is also decomposed into oxalic acid and ammonia by boiling it with caustic alkali. The former unites with the alkali used, while the ammonia passes over, and may be collected as liquid ammonia; the oxalic acid thus generated may be obtained as oxalate of potash if potash be the alkali employed, or as oxalic acid if baryta be used, by decomposing the latter oxalate by means of sulphuric acid. In this case the oxalate of baryta may be treated in the way previously described for oxalate of lead.

As regards these various methods of obtaining oxalic acid, their employment will of course always be a question of £ *s. d.*, the œconomy of many operations of manufacturing chemistry being often dependent upon their adaptation to the requirements or purposes of particular manufacturers, in connexion with other branches of manufacture carried on by them.

The low price at which treacle and sugar are now obtainable is much in favour of their use in this manufacture. The chief point however to which attention must be directed, in order to lessen the cost of production of this article, is in œconomizing the nitric acid used.

In speaking of the action of nitric acid upon sugar, it was observed that carbonic acid is produced, and that it passes off with the deutoxide of nitrogen also set at liberty. The presence of carbonic acid in this case proves a great obstacle in the reconversion of nitric oxide into nitric acid, preventing the union of the oxygen of the air with the nitric oxide. Various processes have been from time to time suggested to effect this œconomy in the manufacture of oxalic acid; amongst these the following may more particularly be noticed:—

In 1846, Mr. Jullion patented a method of converting the oxides of nitrogen, given off in the manufacture of oxalic acid, into nitrous and nitric acids. For this purpose he uses a "generating vessel," which is a vessel something like a Woulf's bottle, only having a moveable top fitting air-tight, and capable of holding about 100

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gallous. The materials to form the oxalic acid are introduced, and the vessel heated by a water-bath (by steam or other convenient means), which surrounds the vessel; a quantity of nitric acid is then added, and air or oxygen is forced in through a pipe inserted in the top. The oxygen, coming in contact with the evolved oxides of nitrogen, immediately converts a portion into nitrous and hyponitrous acids, which are partly again absorbed by the fluid in the vessel; another portion passes off by a pipe inserted in the upper part of the vessel, which pipe passes through a furnace. This part in the furnace is a little enlarged, and is heated to from 600° to 900° F.; this part of the pipe or tube contains spongy platinum, or other similar substances. The gases, on coming in contact with the heated platinum, combine to form nitric acid, which is afterwards condensed in vessels arranged as usual in the manufacture of this acid. Instead of platinum, a close vessel containing water may be used, which decomposes hyponitrous and nitrous acids, giving rise to nitric acid. This principle is applied in the following ways:—The oxides of nitrogen, as evolved from the liquor in the decomposing vessel, coming in contact with oxygen, are converted into hyponitrous and nitrous acids, which, upon being mingled with steam, are decomposed into nitric acid and deutoxide of nitrogen; or the introduction of steam may be obviated by using heated air or oxygen in the decomposing vessels, by which means moisture will be furnished from the liquor; the amount of evaporation thus caused will also prevent an inconvenient increase of the mother-liquor. The compounds thus formed, when passed through suitable condensers, will, if the supply of atmospheric air or oxygen has been in excess, be all or nearly all condensed into nitric acid.

The following is a description of Crane and Jullion's continuous method of manufacturing oxalic acid and nitric acid at one process:—The oxalic acid mother-liquor of a previous process is placed in a closed or covered vessel termed a "generator," formed of slate; nitric acid and syrup in the usual proportions employed for such quantity of mother-liquor, are also placed separately in feeding vessels, over the "generator;" heat is then applied to the mother-liquor, and the temperature raised as quickly as possible to 180° or 200° F. Streams of nitric acid and syrup are then caused to flow into the generator by means of suitable stop-cocks and funnel-pipes, in such a quantity that the delivery of the whole shall occupy about eighteen hours, at the expiration of which time the process will be completed.

The gases arising from the decomposition of the materials so supplied pass off through an eduction-pipe in the top of the generator into a receiver, into which a stream of chlorine is introduced (from a chlorine-generator) sufficient to convert the whole of the oxides of nitrogen into nitric acid. A portion of the water in the receiver is decomposed, its oxygen combining with the oxide of nitrogen to form nitric acid, whilst its hydrogen combines with the chlorine to form hydrochloric acid. These mixed vapours pass over into suitable condensing vessels placed to receive them. The whole of the

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nitric acid and syrup having been run in, and the liberation of the gases or oxides of nitrogen having ceased, the oxalic acid liquor is drawn off from the generator and crystallized.

Messrs. McDougall and Rawson have also patented a method of recovering the vapours which pass off in the manufacture of oxalic acid. To effect this, they direct the employment of a series of vessels containing water, into the first of which the nitrous gas or fumes are passed through a tube dipping below the surface of the vessel; air is also admitted, which mixes with the gas bubbling up through the water. Attached to the last vessel of the series is a pneumatic apparatus, by means of which the mixture of nitrous gas and air is drawn through this series of vessels, each containing a tube dipping into the liquid, and another tube or pipe attached to its top to connect it with the next vessel. The nitrous gas thus passing alternately into air and water, becomes converted into nitric acid. In this process the following reaction is said to take place:—

On $3NO^4$ being passed into water of the temperature of 100° F., or upwards, $2NO^5 + NO^2$ result, the $2NO^5$, *i. e.* 2 atoms of nitric acid, remain in solution, whilst the NO^2, which is an incondensable gas, bubbles through the liquid and unites with the air in the vessel above the liquid; it immediately takes 2 atoms of oxygen from the air and becomes NO^4, which, passing through the liquid, becomes nitric acid and nitrous gas as before; and thus nearly the whole of the nitrous fumes or gas are reconverted into nitric acid.

In Ecarnot's patented process for recovering the nitric acid, he fills his regenerating vessels with a porous substance, such as pumice-stone, supplying the oxygen by a blowing-machine, a flow of steam being brought from a boiler.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

Feb. 2, 1852. (Dr. Lyon Playfair in the Chair.) The following papers were read:—

"On a new Method of obtaining Hippuric Acid in considerable Quantity without Evaporation of the Urine." By Edward Riley, F.C.S., Assistant in the Museum of Practical Geology.

The method described for obtaining hippuric acid consists in adding to fresh cow's urine some hydrochloric acid, in the proportion of half a fluid ounce to a pint of urine. The hippuric acid being very slightly soluble in this acid liquor is deposited, together with some colouring matter, from which it is subsequently purified by dissolving it in water with excess of lime, adding animal charcoal, and heating the mixture for half an hour or more. On adding hydrochloric acid to the filtered liquor, and allowing the mixture to cool slowly, the hippuric acid is deposited in large prismatic cry-

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stals. It sometimes requires to be further purified by repeating this process. The acid thus prepared, on being analysed, gave results agreeing with the established formula for hippuric acid, namely $C^{18} H^9 NO^5 + HO$.

Feb. 16, 1852. (Professor Daubeny, President, in the Chair.) The following papers were read:—

"On the Variation in the relative proportion of Potash and Soda present in certain Samples of Barley grown in Plots of Ground artificially impregnated with one or other of these Alkalies." By Prof. Daubeny.

The author details some experiments, undertaken by him at the Oxford Botanic Garden, with the view of determining whether the usual quantity of potash and soda existing in barley might be made to vary by causing the plant to grow in soil impregnated with more than the ordinary quantity of one or the other of these alkalies.

He found that when the barley had grown in a soil which had been dressed with a strong solution either of carbonate of soda or of chloride of sodium, the ashes of the plant contained about 8 per cent. more soda than was present when the plant had grown in a soil impregnated with carbonate of potash, or left unimpregnated.

This difference may admit of explanation, by supposing one alkali capable of replacing the other within the organism of the plant; but the author thinks it more probable that it arose from the sap circulating through the plant at the time when it was cut, containing in the one case more soda than it did in the other. The saline contents of the fluid of the sap would of course be confounded with those which had been actually assimilated by the plant, and hence, from the variation in its composition, must tend to modify the amount of the alkalies obtained from the ashes of the plant in each instance according to the nature of the material with which the soil had been impregnated.

"On the Compounds of Cotton with the Alkalies." By J. H. Gladstone, Ph.D.

The author first described the process of Mr. Mercer, by which the beautiful fabrics, made known to the public through the Great Exhibition, are produced. When cotton, or an article made of that material, is immersed in strong caustic soda in the cold, a certain combination is effected, which is again destroyed by pure water; but the "Mercerized" cotton thus produced is permanently contracted, and rendered more susceptible of dyes. This was illustrated by a number of specimens, much shrunk, so that they assumed an appearance of extraordinary fineness, others puckered in patterns by partial Mercerization, and others again printed with colours which surpassed in depth and brilliancy the colours produced by the same means on the calico in its original state. Dr. Gladstone proceeded to detail experiments by which he had succeeded in obtaining the compound of cotton and soda free from adhering alkali, through the agency of strong, sometimes absolute alcohol. He found that the proportion of soda which combined with the lignine

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varied with the strength of the solution employed, but under no circumstances exceeded 1 atom, the formula of the "sodaed" cotton being $C^{24} H^{20} O^{20}$, NaO. There was a varying amount of combined water. Some properties of this compound were discussed, and the author then proceeded to state his conviction that there was no sufficient ground for viewing the "Mercerized" cotton as chemically different from the original lignine. It is identical in composition, and the change of properties may be accounted for by the change in its physical condition. When viewed under the microscope, the fibres in their ordinary condition appear as flattened twisted ribands; but the moment they are touched by the alkaline ley, they untwist themselves, contract in length, and swell out, assuming a rounded solid form; and this circular appearance they retain after the soda is removed by water. This not only explains the shrinking, but the cause of a larger quantity of dye being absorbed, as the substance of the fibre itself is porous. Potash has a similar action to that of soda, giving rise to a compound, the formula for which is $C^{24} H^{20} O^{20}$, KO.

Society of Arts.

Feb. 5, 1852. (W. F. Cooke, Esq., Vice-President, in the Chair.) The following paper was read:—

"On the Stearic Candle Manufacture." By Mr. George F. Wilson, Managing Director of Price's Candle Company.

The science of candle-making is indebted for its existence to the eminent French chemist M. Chevreul, who in 1811 began his researches into the nature and constituents of fatty bodies. He discovered that fat, instead of being a simple organic substance, as had been previously believed, was a salt composed of a solid animal acid (margaric) and an animal base (glycerine), the acid being the inflammable part. In 1814, he further discovered the existence of a liquid acid (oleic) existing in lard, and forming a chief ingredient in many fatty bodies. His researches were continued for several years, and in 1823 were given by him to the world in his well-known work. He has recently been presented by the *Société d'Encouragement* with a prize of 12,000 francs.

The first successful attempt to employ commercially these scientific discoveries of Chevreul was that of De Milly of Paris, who commenced manufacturing in 1832. His candles are stamped with the word "Etoile," from the Barrière de l'Etoile, near which his works are situated. De Milly employed a modification of Chevreul's process for separating the acids from the glycerine with which they are combined. Tallow is boiled up with thin cream of lime, which causes the acids to forsake the glycerine and combine with the lime; the acids are then set free by combining the lime with sulphuric acid, and the oleic acid is afterwards separated from the margaric by simple pressure. This is the process of lime "saponification." A large cake of margaric acid, which had been shown by De Milly at the Exhibition, was exposed upon the lecture-table.

The obstacle to the success of this process was its expense, the

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margaric acid requiring nearly 2½ times its weight of tallow to produce it. This obstacle was overcome by the firm of which the lecturer is a member, who in 1830 became possessed of a patent for separating cocoa-nut oil into its solid and liquid parts. In 1831, the candle manufacture was freed from the excise, and received in consequence a great impulse. The success of candles made from cocoa-nut oil was however not great, owing to their requiring snuffing; but it was discovered by Mr. James Wilson, while endeavouring to make cheap candles for the illumination on the occasion of the Queen's marriage, that from a mixture of the cocoa-nut stearine with stearic (pure margaric) acid, candles were produced, which gave a beautiful light and wanted no snuffing. These are the well-known "composite candles."

The next step was the purification of the fat acids by distillation; and the first suggestion of a method of doing this was made by Mr. George Gwynne, who proposed distilling in a vacuum apparatus similar to that used in sugar refining. He afterwards, in conjunction with Mr. George Wilson and Mr. Jones, carried out his idea into practice, by distilling in an atmosphere of steam, which gave the same results as the air-pump, but without its manufacturing difficulties, which were found to be almost insuperable. The process at present employed on the works of the Company is briefly as follows:—The raw material (at present palm-oil) is exposed at a temperature of 350° to the action of about one-twentieth of its weight of sulphuric acid, which has the effect of driving off the glycerine, and of leaving the fat acids free; these acids, which are of a very dark colour, after being washed, are transferred to a still, from which the air is excluded by steam. The distilled material is subjected to pressure, first at the ordinary, and then at a high temperature, and the residue is the material of which the Belmont sperm candles are made. The process of distillation was commenced on a large scale at their works in 1844, two years before the opening of the factory of Messrs. Masse and Tribouillet, the first established for this purpose on the Continent. Arsenic and wax were originally used by Price and Company to destroy the large crystals which were formed in their earlier candles, and which disfigured their exterior; but by pouring the stearic acid into the moulds at its congealing point, instead of at a high temperature, it was found that the crystals were no longer formed. Six kinds of candles are made at the Belmont works:—1. Belmont sperm: of hot-pressed palm acid. 2. Belmont wax: the same material, but coloured with gamboge (to suit the refined prejudices of the home consumers). 3. Best composite: of the same material as 1 and 2, but mixed with cocoa-nut stearine. 4, 5 and 6. Composite 1, 2, 3, of inferior quality. The machinery for making the candles was shown and explained; and as an example of the very large scale of the operations of the Company, it was stated that 800 miles of wick are continually being converted into candles.—*Literary Gazette.*

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THE CHEMICAL GAZETTE.

No. CCXXVII.—April 1, 1852.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Causes of the Agricultural Efficacy of Burnt Clay. By Dr. Augustus Vœlcker, *Professor of Chemistry in the Royal Agricultural College, Cirencester.*

The practice of soil-burning has long since been recommended by different persons as one of the best means of improving stiff clay land, whilst others have denied the utility of soil-burning altogether. But although failures sometimes attended this practice, we are now in possession of numerous incontrovertible instances in which the application of burnt clay was followed by the happiest results. One of the most striking examples in which soil-burning proved highly economical is recorded in vol. vi. p. 477 of the Journal of the Royal Agricultural Society by Mr. Pusey, who very justly observes that burnt clay acts, not merely mechanically, but also as a manure (that is chemically).

The failures attending clay-burning no doubt are due in some cases to carelessness and want of skill on the part of the operator; for it is well known that in over-burning soil, instead of a friable mass, large hard lumps like brickbats are obtained, which on exposure to the atmosphere refuse to fall to powder. Soil burnt at too high a temperature, that is overburnt soil, always proves more or less inefficient. All failures however cannot be attributed to this cause, for it is a fact, attested by practical men well acquainted with the practice of soil-burning, that some kinds of clay after burning do not exhibit the same beneficial effects as others, or none at all, when applied to the land. It becomes therefore an important point to determine what is the nature of those clays which prove efficacious after burning, and what are the characteristics of those clays which are unfit for burning. It is clear however that this question cannot be settled satisfactorily without incurring much expense, as long as we are ignorant of the true cause of the efficacy of burnt clay. In addition to other advantages, the discovery of the cause of the efficacy of burnt clay might probably lead to further improvements in the existing methods of burning clay, which might render them easier, cheaper and more certain.

These and similar considerations, I think, will show at once the practical importance of a fundamental inquiry into the causes of the efficacy of burnt clay.

With a view of contributing something to the solution of the problem, I made some experiments last winter, which have furnished

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me with some interesting analytical results. These, I trust, will throw some light on the rationale of clay-burning, and lead at the same time to a more extensive practice of burning heavy clay land.

In engaging in this inquiry, I proposed to myself several questions, which I shall endeavour to answer successively in the following pages.

1. *What are the Changes produced in Clay by Burning?*

When heavy clay land is burned at a proper temperature, it is materially altered in its physical condition, whilst at the same time the action of the heat produces some chemical changes in the constituents of clay, which appear to me highly important. I shall consider—

I. *The Mechanical Effects of Heat on Clay.*—The mechanical effects of heat on clay are simple and easy to be understood. Heavy stiff clay soils are impervious to water, very tenacious and unctuous, and for these reasons often cold and expensive to work. Clay, when properly burnt, so that it neither melts nor becomes converted into hard stony masses, is rendered harder to some degree, more porous, and under the action of the weather crumbles down to powder without again becoming tenacious or plastic. The application of burnt clay to heavy soils thus tends to make them more open and more friable, and consequently diminishes much the amount of labour in the subsequent working of such soils. The mechanical effects of burnt clay, by which the physical condition of soils is altered so materially, are therefore very important, and by no means to be undervalued in an inquiry into the causes of the efficacy of burnt clay. The beneficial effects of burnt clay are ascribed by many chemists and agricultural writers entirely to its greater porosity, or rather to ammonia, which, according to their views, is absorbed from the atmosphere by burnt clay more extensively than by clay in its natural state. In order to put this theory to the test, I made the following experiments with—

1. Clay, from Huntstile, near Bridgewater, in its natural state.

2. Clay, from the same locality, moderately burnt.

Both portions were moistened with water, and exposed in glass beakers to the atmosphere for a period of two months and twelve days, without however renewing the evaporated water. After that period the quantity of ammonia in each sample was determined by combustion with soda-lime in the usual manner. The following are the results:—

1. Clay, from Huntstile, in its natural state; 239·15 grs. on combustion furnished 4·94 grs. of bichloride of platinum and ammonium; or

100 parts of air-dry clay contained 0·240 per cent. of ammonia (NH^4, O).

2. Clay, from Huntstile, moderately burnt; 210·15 grs. on combustion gave 0·36 of bichloride of platinum and ammonium; or

100 parts of air-dry clay contained 0·019 of ammonia (NH^4, O).

The clay, when unburnt, it will be observed, furnished a much larger quantity of ammonia than the same clay after moderate calcination. We must, however, not conclude that unburnt clay pos-

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sesses a greater power of absorbing ammonia from the atmosphere, for the ammonia obtained in the analysis is partly the result of the decomposition of nitrogenized organic matters which were present in the clay, and which were destroyed on burning.

At all events, the above analyses show that unburnt clay contains ammonia, or the elements from which ammonia is formed, in larger quantities than burnt clay. The quantity of ammonia absorbed by burnt clay besides is so inconsiderable, that it cannot be justly regarded as likely to influence in a sensible degree the fertility of the soil to which burnt clay is applied. For that reason I cannot attach much value to the ammonia theory.

Sprengel ascribes the beneficial action of burnt clay to ammonia, which he says is formed in burnt clay under the influence of protoxide of iron, by the decomposition of water and the nitrogen of the atmosphere. Burnt clay, he thinks, will lose its effects as soon as the protoxide of iron is changed into peroxide, because then the further decomposition of the water and the formation of ammonia cease. I have examined burnt clays which contained no protoxide of iron at all, and which nevertheless were found most efficacious as a manure. This fact alone contradicts Sprengel's theory; but in order to learn if in clay, containing much protoxide of iron, more ammonia is formed than is absorbed by the same clay from the atmosphere, I made the following experiments:—

A portion of clay, from Huntstile, was moderately burnt in a closed crucible, after having been previously mixed with 1 per cent. of charcoal powder. The charcoal powder was mixed with the clay for the purpose of reducing the peroxide of iron in the clay to protoxide.

a. One-half of the clay thus treated was exposed for two months and fourteen days to a dry atmosphere, in a dry state:—

182·81 grs. gave 0·28 grs. of bichloride of platinum and ammonium; or

100 parts gave 0·17 per cent. of ammonia.

b. The other half was thoroughly moistened with water, and exposed for the same length of time to the atmosphere:—

212·11 grs. gave 0·33 grs. of bichloride of platinum and ammonium; or

100 parts gave 0·18 per cent. of ammonia.

These quantities of ammonia are nearly identical. Ammonia accordingly is not formed, as Sprengel supposes, by the decomposition of water, under the influence of protoxide of iron and the atmosphere, in a larger quantity than is absorbed by dry clay from the atmosphere.

Thus under no circumstances do we find ammonia in burnt clay in so large a quantity as to justify us in regarding it as the chief cause of efficacy in burnt clay. The effects of burnt clay cannot be explained by the absorption of ammonia only, nor indeed by the mechanical changes which burnt clay has undergone after burning. In a great measure the efficacy of burnt clay is due to the chemical changes to which the constituents of clays are subject in burning.

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I shall therefore consider—

II. *The Chemical Effects of Heat on Clay.*—In an excellent paper on the effects of burnt clay, Professor Johnston expresses the opinion that the mechanical effects of burning upon clay are insufficient to explain the efficacy of burnt clay; and proves experimentally that clay upon burning is subject to chemical changes, which are of such a kind as to render the constituents of clay more soluble. To these chemical changes the learned professor attaches even more importance than to the mechanical alteration of the condition of the soil.

By my own experiments I am enabled to confirm Johnston's observations respecting the greater solubility of burnt clay, and the diminution of this solubility in over-burnt clay. I have found, further, the important fact, that in burning clay properly, a *large amount of potash is liberated* from the constituents of the clay, and rendered soluble, which existed in the clay before burning in an insoluble state. I am indebted for the material with which my experiments were made to Sir Thomas Tancred, who procured for me some clay of the new red sandstone formation, from the farm of Huntstile, near Bridgewater, tenanted by Mr. Thomas Danger.

The nature of the chemical changes which may be supposed to affect the action of burnt clay on the land to which it is applied was examined by four distinct analyses:—

No. I. Clay-soil in its natural state.

No. II. A quantity of the same clay-soil was exposed to a *dull* red heat in a *closed* platinum crucible, and kept at that temperature for half an hour. The clay, after burning, had a dark gray colour.

No. III. Another portion of the same clay-soil was exposed to a red heat for half an hour in an open crucible. The contents of the crucible were frequently stirred with a platinum wire, in order to effect the complete combustion of the organic matters, and to secure the perfect oxidation of any protoxide of iron which was present in the clay. After burning, the colour of this portion of the clay was red, rather brighter than the natural colour of the soil.

No. IV. A fourth portion of the same clay-soil was exposed for about three hours to a full red heat in an open crucible.

As water, saturated with carbonic acid, produces the same effects on the constituents of clay as dilute acid, and acts only slower, I preferred to apply dilute muriatic acid, instead of water charged with carbonic acid, in order to test the solubility of the above four samples of clay. Accordingly, separate quantities of Nos. I., II., III., and IV. were boiled for half an hour in 4 oz. of dilute acid, containing one-tenth of its bulk of hydrochloric acid. The insoluble part of the clay was collected on a filter, and washed with distilled water until nothing more was dissolved.

In the soluble part of Nos. I., II., III., and IV. the following substances were determined quantitatively:—Soluble silica, oxide of iron and alumina, carbonate of lime, potash, soda and phosphoric acid.

In No. IV. phosphoric acid was not determined.

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The following table exhibits the results of these several analyses:—

Clay from Hartstile, near Bridgewater.	No. I.	No. II.	No. III.	No. IV.
Water driven off at 212° F.	5·539	9·160	9·200	9·300
Organic matter and water of combination	3·621			
Insoluble matter (in dilute hydrochloric acid).....	84·100	80·260	81·845	85·30
Soluble matter, consisting of—				
Soluble silica	1·450	1·380	1·580	1·150
Oxides of iron and alumina ..	3·070	3·245	6·092	2·970
Carbonate of lime	0·740	0·420	0·550	0·188
Potash	0·269	0·941	0·512	0·544
Soda	0·220	0·336	0·314	0.104
Phosphoric acid.....	0·380	0·165	0·128	undeter.
Chlorine and sulphuric acid ..	traces	traces	traces	traces
Magnesia (not determined)				
	99·389	100·907	100·221	99·565
On combustion with soda-lime, ammonia (NH^4,O) produced in	0·240	0·019	..	0·008
		0·017		
		0·018		

These analytical results give rise to the following suggestions:—

1. That, after burning, this clay has become much more soluble than clay in its natural state.

2. They not only teach generally that clay becomes more soluble in burning, but that the temperature to which it is exposed mainly regulates the solubility of the clay. A proper temperature for burning clay is indeed a condition in the process on which the success of the operation chiefly depends. We see, from the preceding tabulated results, that 100 parts of clay, in its natural state, furnishes only 6·74 grs. of soluble inorganic matter, leaving 84·100 insoluble behind; whilst the same clay, burnt at a temperature and under circumstances in which the organic matter was not altogether destroyed, left 80·260 of insoluble matters. An increase of the temperature, sufficiently high to burn off the small amount of organic matter which enters into the composition of this clay, had the effect of reducing the solubility of its constituents to about 1½ per cent.; and a more protracted exposure to a still higher temperature had the effect of a further reduction of its solubility to such an extent that this over-burnt clay became less soluble than the same clay in its natural state:—

	Proportions of soluble inorganic matters.	Proportions of insoluble inorganic matters.
Clay, No. I. (unburnt)	6·740	84·100
Clay, No. II. (slightly burnt)	10·580	80·260
Clay, No. III. (burnt more than II.).	8·955	81·845
Clay, No. IV. (over-burnt)	5·391	85·309

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3. The above analyses distinctly prove the important fact, to which I would invite particular attention, that the *alkalies*, more particularly *potash*, are rendered *soluble* to a considerable extent in the process of burning.

The temperature to which the clay has been exposed here regulates the proportion of potash rendered soluble in dilute hydrochloric acid in a remarkable manner.

In the natural clay, only 0·269 per cent. of potash were soluble; whereas in clay burnt at a moderate heat, and under circumstances resembling those under which clay is burnt in the field, the quantity of soluble potash amounted to more than three times the former quantity. In clay No. II., the higher temperature to which it was exposed caused a diminution in the proportion of soluble potash; and in No. III. nearly the same quantity of potash as in No. IV. was obtained:—

	Proportions of soluble potash.
Clay, No. I. (actual state)	0·269
Clay, No. II. (slightly burnt)	0·941
Clay, No. III. (burnt more strongly)	0·512
Clay, No. IV. (over-burnt)	0·544

The actual quantities of soda rendered more soluble in burning are trifling, but still sufficiently large to confirm the fact that soda is rendered more soluble in burning. The higher temperature applied in burning Nos. III. and IV. likewise was attended with a slight diminution of soluble soda:—

	Proportions of soluble soda.
Clay, No. I.	0·220
Clay, No. II.	0·336
Clay, No. III.	0·314
Clay, No. IV.	0·104

4. A reference to the tabulated analytical results further shows, that the relative quantities of lime in the soluble portion of each vary considerably:—

	Proportion of soluble lime, calculated as carbonate.
Clay, No. I.	0·740
Clay, No. II	0·420
Clay, No. III.	0·550
Clay, No. IV.	0·188

The three latter quantities are marked down in the analyses as carbonate of lime, for the sake of comparison with No. I., in which the lime really existed as carbonate of lime; but as not the slightest effervescence took place on dissolving the burnt clay in dilute muriatic acid, it is clear that the lime did not exist in the state of carbonate. The lime must have existed in Nos. II., III., and IV. as caustic lime, or in the state of silicate.

The excess in analyses Nos. II., III., and IV. is partly due to this inaccuracy of stating the results, partly to the fact that silicate of protoxide of iron in burning becomes decomposed. The protoxide of iron is rendered soluble in dilute muriatic acid, but in the ana-

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lyses it is obtained and calculated as peroxide; hence we find the largest excess in No. II., in which most iron has become soluble in dilute acid after burning.

The following considerations, which at the same time explain the mode in which potash is liberated from the constituents of clay and rendered soluble, induce me to think that the lime in Nos. II., III., and IV. existed in a state of silicate. The usual method of determining the quantity of potash and soda in insoluble silicates consists in fusing the finely-powdered substance with an excess of carbonate of baryta. In this process, potash and soda are rendered soluble in the following manner:—The baryta combines with the silica, originally present in combination with potash and soda; silicate of baryta is formed, and the alkalies potash and soda uniting with the carbonic acid of the carbonate of baryta, are rendered soluble.

Lime, which in its chemical relations is closely allied to baryta, acts precisely in the same manner on insoluble silicates of potash and soda. If clay originally contains carbonate of lime, it will act at an elevated temperature on the insoluble silicates of potash and soda, present in many clays in the form of fragments of felspar or mica; and by double decomposition it will give rise to the production of silicate of lime and carbonate of potash. Silica enters into combination with lime in different proportions; some of these combinations are soluble in dilute acids, most of them are insoluble. Instead of carbonate of lime and insoluble silicate of potash, we thus find in burnt clay a larger proportion of soluble potash and silicate of lime, which is partly insoluble in dilute acids. The diminution of the quantity of lime, and the more abundant proportion of potash in the soluble part of burnt clay, thus find a ready explanation. Much, however, as indicated by the practical observations and the above analytical results, depends on the proper regulation of the temperature.

2. How does Burnt Clay act in improving the Soils; or, in other words, what are the causes of the efficacy of Burnt Clay?

The answer to this question will become much more intelligible after we shall have considered briefly the origin and composition of agricultural clays, and pointed out those substances in clays on which their fertilizing properties chiefly depend.

Clays generally result from the disintegration and degradation of granitic and felspathic rocks. Felspar, a mineral composed of silicate of potash or soda and silicate of alumina, exposed for a long time to the united action of the atmosphere and water, suffers a gradual decomposition, and falls altogether to powder. Silicate of potash, a soluble salt, is worked out by the rain falling on the decomposed rock, and converted in its turn, by the carbonic acid of the atmosphere, into carbonate of potash and silica, which remains behind in a gelatinous or soluble state with insoluble silicate of alumina, the chief constituent of clays. The analyses of different samples of agricultural clays exhibit many differences in their com-

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position, and show that agricultural clays are never pure silicate of alumina, but mixtures of pure clay (silicate of alumina) with more or less sand, undecomposed fragments of felspar, mica, granite, and other minerals, carbonate of lime, magnesia, free or uncombined alumina, oxide of iron, soluble silicate of potash, traces of phosphoric and sulphuric acid and chlorine. In some clays lime occurs in so large quantities, that on this account they cannot be used for the making of tiles. Of such a kind is Bradford clay, from the neighbourhood of Cirencester, in which I have found no less than 19·92 per cent. of carbonate of lime. In others, little lime, but considerable quantities of free alumina and oxide of iron are found. To this kind of clays belongs an agricultural clay, the analysis of which I subjoin, in order to show its complex composition:—

Analysis of Clay from Huntstile Farm, near Bridgewater.

Water of combination, and a little organic matter	3·38
Insoluble siliceous matter (fine clay)	54·89
Finely-divided silica (soluble in dilute caustic potash)..	17·94
Oxides of iron	8·82
Alumina	6·67
Lime	1·44
Magnesia	0·92
Phosphoric acid	0·51
Potash	1·48
Soda	1·08
Traces of sulphuric acid and chlorine, carbonic acid, and loss	2·87
	100·00

On these foreign admixtures, which all agricultural clays contain, and the state of division of the sand and other constituents, the plasticity, tenacity, porosity, and other physical characters depend. In an examination of an agricultural clay, therefore, not merely its ultimate chemical composition should be ascertained, but likewise its mechanical condition. This has been done with a sample of plastic clay from Coldash Common, near Newbury, which I owe to the kindness of Mr. Robert Brown, of Cirencester. By washing carefully clay with water, and collecting the deposit which subsides from the muddy liquid at different intervals, a tolerably good idea of the state of division of the clay can be formed:—

Analysis of Plastic Clay from Coldash Common, near Newbury, Berkshire.

1. Mechanical Examination.

100 parts of this clay contain—

Fine quartz sand, deposited after five minutes.....	54·64
Clay, with a little very fine sand, deposited after ten minutes	10·52
Fine clay, deposited after fifteen minutes.....	2·57
Finest clay, remaining suspended in water after the lapse of a quarter of an hour.....	32·27
	100·00

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2. Chemical Examination.

a. *General Analysis.*

Water of combination, and a little organic matter....	8·698
Sand.....	54·640
Pure clay.....	25·462
Oxides of iron and alumina, lime, and other substances, soluble in acids.....	11·200
	100·000

b. *Detailed Analysis.*

Water of combination, with a little organic matter ..		8·698
Silica.....		73·736
Soluble oxides of iron and alumina	5·031	12·198
Insoluble	7·107	
Lime.....		2·980
Magnesia		0·047
Potash		2·077
Soda.....		0·525
Chlorine		a trace
		100·201

Not only the mechanical state of division, and the relative proportions of the foreign admixtures which are found in agricultural clays, influence their characters, but also the state of combination in which the constituents of such clays occur, materially alters their properties. In the subjoined analyses of three samples of clays from Dumbelton, Gloucestershire, made in my laboratory, care has been taken to ascertain the state of combination in which the constituents of these clays are likely to occur:—

Clays from Dumbelton.

	No. I.	No. II.	No. III.
Water of combination and organic matter....	7·69	6·62	6·68
Oxides of iron.....	8·24	7·33	8·63
Alumina, soluble in acids	8·04	10·62	9·25
Alumina, in a state of silicate	10·04	7·06	9·66
Lime, carbonate of.....	1·12	0·70	0·19
Lime, in a state of insoluble silicate	0·44	0·54	0·24
Magnesia, soluble in acids.....	0·62	0·12	0·56
Magnesia, in a state of insoluble silicate	0·34	0·39	0·34
Potash and soda, soluble in acids	0·73	1·04	1·13
Potash and soda, in a state of insoluble silicate	0·94	2·70	1·82
Silica (soluble in acids).....	0·09	0·06	0·08
Silica (insoluble in acids)	61·71	62·82	61·42
	100·00	100·00	100·00

Having given a brief outline of the origin and composition of agricultural clays, let us see, in the next place, on which of their constituents their fertilizing powers depend.

In a chemical point of view, silicate of alumina (pure clay) does

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not contribute in itself to the direct nutrition of plants, as it is not found in the ashes of cultivated plants. We must look therefore for the direct fertilizers of clays amongst the accessory or foreign ingredients of agricultural clays. Of these, lime, magnesia, sulphuric acid, silica, and chlorine are indeed essential to the growth of plants; but as these substances are found in most soils, or can be supplied at a cheap rate when deficient, the chief value of an agricultural clay depends on the proportion of phosphoric acid and potash and soda which it contains. Potash in particular is an essential element in all ashes of plants, and acts as a most powerful manure. The chief source of potash in ordinary soils is the clay, which enters into the composition of almost all soils. Clay, we have seen, is in many cases derived from felspar, a double silicate of alumina and silicate of potash, and frequently contains some undecomposed fragments of felspar or similar minerals; from which, under the action of the weather, potash is liberated, and rendered available to plants. The large amount of felspar and similarly composed minerals, in some clays, thus furnishes an almost inexhaustible supply, from which plants may derive their potash. Plants however can only avail themselves of the soluble potash which exists in clays, and not of the potash which occurs in them in the form of felspar. But as the soluble potash in clay soil sooner or later will be exhausted by the removal of the crops grown upon it, the soil gradually becomes more and more sterile, and at last refuses to grow any remunerative crop. The natural fertility of exhausted soil is then restored again by the process of fallowing. By that process a fresh portion of the soil, not hitherto exposed to the action of the atmosphere, is brought up; and, amongst other changes, the undecomposed fragments of felspar are forced, by the combined action of air and water, to yield their potash and soda, which are the indispensable requisites of a healthy vegetation.

In an age of railway and steam enterprise and telegraphic dispatch, agriculture is forced to progress, and, in consequence of this, fallowing must necessarily yield to some more extensive and expeditious means of gaining the same advantages. Soil-burning is one of these means. The above-mentioned analyses have taught me, that, in burning clay, a large proportion of potash, which existed before in an insoluble state, is liberated and rendered available for immediate use by plants. In burning clay, then, similar changes are effected in a few days, which in mere fallowing are produced in as many months. To this *liberated potash* I am inclined to ascribe the *chief efficacy* of burnt clay, without however considering the mechanical changes clay undergoes in burning as unimportant.

The fact that felspar is more readily decomposed after having been moderately calcined is not a new one, Professor Fuchs of Munich, having shown clearly that this is the case not only with felspar, but also with other minerals, into the composition of which silicate of potash enters. Fully in accordance with this fact is the practical observation of Professor Lampadius, who found, by a series

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of field experiments, that moderately-calcined gneiss, granite, certain kinds of porphyry and trap rocks, all of which contain silicate of potash like burnt clay, promote the luxuriant growth of many plants in a remarkable manner.

Phosphoric acid, the only other valuable constituent of agricultural clays, is not rendered more soluble by burning, but rather the contrary; the efficacy of burnt clay, therefore, cannot be due to phosphoric acid.

I have shown above in what manner lime appears to me instrumental in liberating the potash of clays. If this explanation of the action of lime on silicate of potash is true, we can easily conceive how the addition of lime to clay, originally poor in this element, will increase the amount of soluble potash and soda. I would therefore suggest the application of quick-lime to newly-burnt clay land, or the mixing of clay with lime before burning, as likely to be attended with most beneficial effects. The explanation of the action of lime on clay, and the suggestion I have thrown out, are supported by an observation of Professor Fuchs, of Munich, to which particular interest attaches. This distinguished man found, that when felspar is moderately burnt, and in a powdered state is boiled with quick-lime and water for a short time, or even digested in the cold with quick-lime and water for a longer period, so large a proportion of potash is liberated from the constituents of felspar, that on these grounds he recommended a process of extracting and manufacturing potash on a large scale from felspar. He has shown, that, under these circumstances, insoluble silicate of lime and soluble carbonate of potash are formed.

3. *By what Qualities or Characteristics are Clays totally unfit for Burning distinguished from those which prove most efficacious after Burning?*

Pure clays, such as pipe and porcelain clay, consist almost entirely of silica and alumina; and as silicate of alumina does not itself serve as direct food for plants, they are found to be sterile in their natural state, and will remain so after burning. On the other hand, the more undecomposed potash in the shape of felspar or any other mineral a clay contains, the more useful it will be found after burning. In support of the theory I have embraced, with respect to the efficacy of burnt clay, it may be mentioned that I have determined the whole amount of alkalies which the clay from Huntstile farm contained in any form. The greater part of the potash and soda in this clay is present in the state of insoluble silicate; and as I find no less than 4·726 per cent. of potash and 0·88 per cent. of soda, I have no hesitation in suggesting that this clay is most likely to prove very efficacious after burning. With this theoretical speculation agrees well the fact mentioned by Mr. Danger, the tenant of Huntstile farm, that by burning this clay the land is very much improved. Mr. Danger says:—"Of course I can only speak to the fact. A soil, which I have found *quite sterile*, on which this process has been used, became *totally changed*."

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4. *Can it be determined by Chemical Analysis, whether Burning will be efficacious in rendering Clay a Fertilizer or not?*

From the preceding remarks it follows, that the fertilizing effects of clay mainly depend on the proportion of potash which it contains; and as any good analytical chemist may determine the exact quantity of potash which may be extracted from a clay, we possess the means of deciding at once whether a clay is likely to be efficacious or not.

5. *What are the reasons of the Failures attending Overburning?*

Professor Johnston has already shown, that, in overburning the constituents of clay, they are rendered less soluble than when properly burnt. My own experiments fully confirm the Professor's observations. Overburnt clay, I have found farther, does not absorb so much ammonia from the atmosphere as properly burnt clay, which is easily explained by the diminished porosity, and consequently diminished absorptive power of such clays.

A portion of overburnt clay from Huntstile was exposed to the atmosphere, moistened with water, for two months and thirteen days. The amount of ammonia absorbed by the clay was then determined by combustion with soda-lime. 219 grs. of air-dry clay gave 0·155 grs. of bichloride of platinum and ammonium, or 100 parts furnished only 0·008 per cent. of ammonia. Moderately burnt clay will absorb double the quantity of ammonia from the atmosphere, which will be absorbed by overburnt clay under precisely the same circumstances. The causes of the failures attending overburning I am therefore inclined to ascribe,—1st, to the mechanical changes clay undergoes in burning; 2nd, to the chemical changes which render such clays less soluble; 3rd, to the diminished power of absorbing ammonia from the atmosphere.

6. *What is the reason that Burnt Clays improve especially Root-Crops?*

All root-crops, such as turnips, carrots, swedes, mangolds, potatoes, &c., require much potash as a necessary article of food. The ashes of these plants contain about half their weight of potash. Mr. Woodward's observation, that root-crops are particularly benefited by burnt clay, thus receives an easy explanation from the mode of its action, which I have endeavoured to explain in the preceding pages.—From the *Journal of the Royal Agricultural Society of England*, vol. xii. part 2.

On the Combinations of Carbonic Acid and Water with Oxides of Cobalt and Nickel. By H. Rose.

When a solution of sulphate of cobalt is heated with carbonate of soda, a precipitate is formed having the composition $2CoO, CO^2 + 3CoO, HO + HO$, in which the carbonate and the hydrate are combined with no slight affinity, as it is obtained of the same composition when precipitated from concentrated as from dilute solu-

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tions in the cold, and even from concentrated solutions at a boiling temperature. But it always contains some sulphuric acid as an insoluble basic salt. It is only when dilute solutions are decomposed at the boiling-point that a precipitate is obtained which approximates to the composition $CoO, CO^2 + 2CoO, HO + HO$. With regard to all the precipitates formed by carbonated alkalies from solutions of oxide of cobalt, it is to be remarked that they are remarkably difficult to wash.

If the solution of sulphate of cobalt is treated with an excess of bicarbonate of potash in the cold, there is formed, with brisk evolution of carbonic acid, a voluminous precipitate, which by long standing is transformed into a heap of tolerably distinct crystals having the composition $KO, CO^2 + CoO, CO^2 + 10HO$, a compound which Deville has prepared a short time since. But the preparation of this remarkable double salt does not always succeed, as the two salts of which it consists are combined with only a very slight affinity. If, for instance, the solutions of the decomposing salts are employed more dilute, or if bicarbonate of soda is used, there is obtained after long standing a body having the composition $CoO, HO + 10CoO, CO^2$.

The compound of carbonate of cobalt with the hydrated oxide, $2CoO, CO^2 + 3CoO, HO + HO$ becomes dark brown at 302° F. The hydrated oxide then passes into hydrated peroxide, but the carbonated oxide remains unaltered. At 392° F., however, it assumes a deep black colour, and is converted into a hydrated peroxide of the composition $HO, 4Co^2 O^3$.

The oxide of nickel separates from the solution of sulphate by means of carbonate of soda as a compound having the composition $2NiO, CO^2 + 3NiO, HO + 2HO$, as well when concentrated as when dilute solutions are mixed together. Even at the boiling temperature, concentrated solutions give a precipitate of almost the same composition, and it is only when dilute solutions are decomposed at the boiling temperature that much carbonic acid is driven out.

By treating a solution of sulphate of nickel with bicarbonate of potash, a distinctly crystalline double salt is obtained having the composition $KO, 2CO^2 + NiO, CO^2 + 10HO$, but by carbonate of soda only an uncrystalline compound of $NiO, HO + 5NiO, CO^2$.

When the compound $2NiO, CO^2 + 3NiO, HO + 2HO$ is heated to 302° F., no peroxide is formed; it merely loses a little carbonic acid. At 392° F. some peroxide is formed, but it retains at this temperature almost the entire quantity of carbonic acid which was left at 302° F. It does not lose all the carbonic acid until the temperature reaches 572° F., and is then converted into a black powder having the composition $HO, Ni^2 O^3 + 6NiO$.—*Bericht der Acad. der Wissens. zu Berlin*, 1851.

Magnesia as an Antidote to Salts of Copper. *By* M. Roucha.

M. Roucha has published in the 'Gazette Médicale de Strasbourg' some observations which tend to prove—

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1. That calcined magnesia completely arrests the symptoms of poisoning by sulphate of copper, when it is administered sufficiently soon after the introduction of the poison.

2. That the dose of magnesia necessary to neutralize the effects of this salt of copper is at least 8 parts of the antidote to 1 of the sulphate.

3. That, as the magnesia behaves towards other salts of copper as it does to the sulphate, preceding the formation of a soluble copper compound in its presence, it is very probable that it will serve as an antidote to all the salts of copper.—*Journ. de Pharm. et de Chim.*, Nov. 1851; and *Monthly Journal of Medical Science*, March 1852.

Further Researches on the Colouring Matters of Fustic. By Prof. R. Wagner.

The author has continued his investigations on the colouring principle of *Morus tinctoria*. The following are the results of his last communication on the subject:—

1. Oxyphenic acid (phenic acid) is identical with pyrocatechine.

2. Oxyphenic acid appears to be a frequent product of the dry distillation of different organic bodies.

3. Oxyphenic acid stands in the same relation to oxypicric acid as phenylous acid to nitrophenissic acid (picric acid).

4. Oxypicric acid is oxyphenic acid in which 3 equivs. H have been replaced by 3 equivs. NO^4. It is consequently trinitrooxyphenic acid.

5. Oxyphenic acid yields, as the final product of the action of chlorine, chloranile (quadrichlorquinone).

6. The monochlorinated niceic acid of St. Evre is chloroxyphenic acid, and the first member of a series of chlorinated products originating from oxyphenic acid, the last of which is chloranile.

7. The hypothetical niceic acid of St. Evre and the *acide phénilique* of Laurent have been obtained by the finding of oxyphenic acid.

In his former papers on the colouring matters of fustic*, the author stated, that in the dry distillation of moritannic acid, morine and rufimoric acid, the pyro acid obtained, to which he then gave the name of phenic acid, but which is now called oxyphenic acid (that is, phenylous acid + $O^2 = C^{12} H^6 O^4$), had the same composition and many of the properties of the pyrocatechine discovered by Zwenger. It therefore became necessary to prepare some pyrocatechine, and to submit it to a comparative examination with reference to oxyphenic acid.

In order to prepare the pyrocatechine, powdered catechu was submitted to dry distillation; the liquid, which passed over in considerable quantity, was of a brownish colour, had a strong acid reaction, and smelt like a mixture of wood-vinegar and acetone. It was left to evaporate spontaneously; in the course of several days it had become converted into a black crystalline mass, which

* Chem. Gaz., vol. ix. pp. 1, 21, 241, 266.

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was freed from adherent tar by pressure between bibulous paper, and purified by repeated sublimation.

The pyrocatechine thus prepared formed, after sublimation, broad, very shining white plates, which had a bitter pungent taste, and an odour somewhat resembling phenylous acid. The solutions in water and alcohol had a slightly acid reaction. A deal-shaving, immersed in hydrochloric or nitric acid, was coloured violet by the concentrated aqueous solution of the pyrocatechine, just as by that of oxyphenic acid. The crystals, dried at 176° F., melt at 230°–239° (259° according to Zwenger). The crystals however begin to evaporate at 122°–140°. The fused pyrocatechine boiled violently between 464° and 482°. Pyrocatechine separates from concentrated aqueous solutions in small rectangular prisms; its aqueous solution behaves towards chloride of gold, nitrate of silver, chloride of platinum, perchloride of iron, ammonia, potash, and baryta water precisely like the aqueous solution of oxyphenic acid.

To prepare the compound of pyrocatechine with oxide of lead, an alcoholic solution of pyrocatechine was precipitated with an alcoholic solution of neutral acetate of lead. The bulky white precipitate was washed with boiling alcohol, and then dried under the receiver of an air-pump; when dry, it formed a white powder, with a slight tint of green. The following numbers were obtained on analysis, and are arranged for comparison with the author's analyses of pyromoritannic acid:—

		Pyromoritannic acid.					
	Pyrocatechine.	I.	II.	III.			
Carbon.....	65·32	65·51	65·45	65·61	12	=72	65·45
Hydrogen	5·64	5·86	5·62	5·68	6	6	5·46
Oxygen	..	..	..	..	4	32	29·09

From the above analyses it follows that pyrocatechine is identical with pyromoritannic or oxyphenic acid. Oxyphenic acid is bibasic; the formula of its salts appears to be $C^{12}(H^4R^2)O^4$.

In a former notice the author pointed to the circumstance, that oxyphenic acid, $C^{12}H^6O^4$, differed in respect to its composition from the formulæ of saligenine and orcine ($C^{14}H^8O^4$) only by $-C^2H^2$. Experiments made with a view to ascertain which of these two bodies is homologous with oxyphenic acid, have led to no result. But it appears as if a third substance, the pyroguaiacic acid, $C^{14}H^8O^4$, of Sobrero, Pelletier and Deville, which is isomeric with saligenine and orcine, and which substance, in respect to its products of decomposition, appears to have many properties in common with oxyphenic acid, is homologous with it.

When a mixture of chlorate of potash and hydrochloric acid is allowed to act upon oxyphenic acid, an exceedingly violent reaction ensues. The liquid turns dark red, and deposits after some time yellowish flakes, which have a peculiar odour, separate from the alcoholic solution in crystalline laminæ, and can be sublimed unaltered. This substance appeared to be chloranile, $C^{12}Cl^4O^4$—

$C^{12}H^6O^4$, oxyphenic acid $+6Cl = C^{12}Cl^4O^4$, chloranile $+2ClH$.

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If chloranile were not a frequent final product of the action of chlorine upon organic substances, the formation of chloranile from oxyphenic acid might lead to the suspicion that the latter acid stood in some relation to the isomeric hydroquinone and the quinone substances in general, since Städeler obtained from quinone, by the action of chlorine, the substances mono-, bi-, tri- and quadrichloroquinone. This latter substance is however chloranile.

The action of chlorine upon oxyphenic acid is so violent that it cannot be regulated, and no intermediate product could be obtained. Should it be possible to conduct the reaction so that an exchange of hydrogen for chlorine take place equivalent for equivalent, we should obtain an acid with the formula—

$$C^{12}H^5ClO^4 = C^{12}\left\{\begin{matrix}H^5\\Cl\end{matrix}\right\}O^4.$$

This acid however has already been prepared in a different manner by St. Evre, viz. by the action of chlorine upon benzoate of potash, and has been called monochlorinated niceic acid. Its name should now be monochloroxyphenic acid. St. Evre further obtained an acid, which is derived from oxyphenic acid by 1 equiv. hydrogen being replaced by 1 equiv. chlorine, whilst a second equiv. hydrogen has been replaced by 1 equiv. hyponitric acid; therefore—

$$C^{12}\left\{\begin{matrix}H^4\\Cl\\NO^4\end{matrix}\right\}O^4.$$

To this acid St. Evre applied the name of nitrochloroniceic acid; the author calls it nitrochloroxyphenic acid. St. Evre suspected a connexion between his acid and phenic acid (phenole, phenylous acid), $C^{12}H^6O^2$; in the description of the monochlorinated niceic acid, he states, that, on supposing the chlorine replaced by hydrogen, we should obtain the substance $C^{12}H^6O^4$. Admitting the formula of the alcohol of the phenyle series to be $C^{12}H^6O^2$, this latter substance would stand in the same relation to the acid in question as an aldehyde to the acid which is formed from it by the absorption of 2 equivs. oxygen.

When oxyphenic acid is treated with nitric acid, there is obtained, according to Wagner, oxalic acid and a nitro-acid; the latter is likewise formed when oxyphenic acid is added to a mixture of nitric and fuming sulphuric acids. He was unable to ascertain the composition and the nature of the nitro-acid, but it was evidently not picric acid. But since, by the action of nitric acid upon morine, oxypicric acid is formed, and oxyphenic acid is apparently produced in the dry distillation of all those substances which yield oxypicric acid on oxidation with nitric acid, and further an intimate connexion exists between oxyphenic and oxypicric acids, it may be assumed that the acid produced in the action of nitric acid upon oxyphenic acid is oxypicric acid.

All those acids to which the name of conjugate nitric acids was formerly applied, are, according to recent investigations, derivatives from non-nitrogenous acids, in which one or more equivs. hydrogen

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have been replaced by an equal number of equivs. of hyponitric acid (NO^4). Thus picric acid is phenylous acid, $C^{12} H^6 O^2$, in which a substitution of 3 equivs. NO^4 for 3 equivs. H has taken place:—

$$C^{12} H^3 N^3 O^{14} = C^{12} \left\{ \begin{matrix} H^3 \\ 3NO^4 \end{matrix} \right\} O^2.$$

Picric acid is consequently trinitrophenylous acid, in the same manner as the substance $C^{12} H^5 NO^6$, prepared by Hofmann by treating phenylous acid with nitrous acid, is mononitrophenylous acid, and nitrophenissic acid, $C^{12} H^4 N^2 O^{13}$, is dinitrophenylous acid. In the same manner anilic acid, $C^{14} H^5 NO^{10}$, originates by substitution from salicylic acid, $C^{14} H^6 O^6$, and the mono-, di- and trinitroanisic acids from anisic acid, &c.

Of the so-called conjugate nitric acids there was only one, viz. the oxypicric acid of Erdmann (styphnic acid, Will), $C^{12} H^3 N^3 O^{16}$, the constitution of which was still unknown, from the corresponding non-nitrogenous acid being wanting. But this acid has now been discovered; it is the pyrocatechine of Zwenger, the oxyphenic acid discovered by the author among the products of decomposition of moritannic acid, morine and rufimoric acid.

Oxypicric acid is formed from oxyphenic acid just in the same way as picric acid is produced from phenylous acid:—

$C^{12} H^6 O^4$, oxyphenic acid $+ 3NO^5 = 3HO + C^{12} H^3 N^3 O^{16}$, oxypicric acid.

Consequently oxypicric acid is oxyphenic acid in which 3 equivs. hydrogen have been replaced by 3 equivs. hyponitric acid—

$$C^{12} H^3 N^3 O^{16} = C^{12} \left\{ \begin{matrix} H^3 \\ 3NO^4 \end{matrix} \right\} O^4.$$

It follows from what has been stated above, that with respect to its relative constitution oxypicric acid does not differ from the other nitro-acids. The author, speaking of the nitro-acids in general, opposes the view that NO^5 enters into organic compounds. The only compounds, it is true, in which the existence of nitric acid is still admitted by some chemists are xyloidine, pyroxyline and nitromannite. The formulæ of the two first substances may be made to agree perfectly with the assumption of hyponitric acid starting from the formula $C^{12} H^{10} O^{10}$. In this case xyloidine is the binitro-compound—

$$C^{12} \left\{ \begin{matrix} H^8 \\ 2NO^4 \end{matrix} \right\} O^{10},$$

pyroxyline the trinitro-compound—

$$C^{12} \left\{ \begin{matrix} H^7 \\ 3NO^4 \end{matrix} \right\} O^{10}.$$

With respect to nitromannite, the formula

$$C^6 \left\{ \begin{matrix} H^4 \\ 3NO^4 \end{matrix} \right\} O^6, \text{ trinitromannite,}$$

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appears to him to be more correct than $C^{12}H^8O^6+6NO^5$. The reasons advanced by Knop for this view the author considers unsatisfactory, and mentions in opposition that hitherto no bases have been prepared from pyroxyline, xyloidine or nitromannite; and that Zinin's process can only be applied in the case of such nitrated substances which either contain no oxygen, as nitrobenzole, nitrotoluole, nitroxylole, nitrocumole, &c., or contain it in such a form that it cannot be removed by the action of strong bases in the form of carbonic acid, such as nitroanisole, nitrophenetole, &c.

Derivatives of Oxyphenic Acid.—Arranging together the results of the author's examination and those of St. Evre on oxyphenic acid and its derivatives, we obtain the following series of substances:—

Oxyphenic acid (pyrocatechine, niceic acid)	$C^{12}H^6O^4$	(prepared)
Monochloroxyphenic (chloroniceic acid)	$C^{12}\left\{\begin{matrix}H^5\\Cl\end{matrix}\right\}O^4$	(prepared)
Dichloroxyphenic acid	$C^{12}\left\{\begin{matrix}H^4\\Cl^2\end{matrix}\right\}O^4$	(unknown)
Trichloroxyphenic acid	$C^{12}\left\{\begin{matrix}H^3\\Cl^3\end{matrix}\right\}O^4$	(unknown)
Chloranile (quadrichloroquinon)	$C^{12}Cl^4O^4$	(prepared)
Nitrochloroxyphenic acid	$C^{12}\left\{\begin{matrix}H^4\\Cl\\NO^4\end{matrix}\right\}O^4$	(prepared)
Mononitroxyphenic acid	$C^{12}\left\{\begin{matrix}H^5\\NO^4\end{matrix}\right\}O^4$	(unknown)
Dinitroxyphenic acid	$C^{12}\left\{\begin{matrix}H^4\\2NO^4\end{matrix}\right\}O^4$	(unknown)
Trinitroxyphenic (oxypicric, styphnic) acid	$C^{12}\left\{\begin{matrix}H^3\\3NO^4\end{matrix}\right\}O^4$	(prepared)
Nicene (phenylene)	$C^{10}H^6=(C^{10}H^5)H$	(prepared)
Chloronicene	$C^{15}\left\{\begin{matrix}H^5\\Cl\end{matrix}\right\}$	(prepared)
Nitrochlonicene	$C^{16}\left\{\begin{matrix}H^4\\Cl\\NO^4\end{matrix}\right\}$	(prepared)
Chloronicine (isomeric with chlorinated nicotine)	$C^{10}\left\{\begin{matrix}H^6\\Cl\end{matrix}\right\}N$	(prepared)
Paranicene	$C^{20}H^{12}$	(prepared)
Nitroparanicene	$C^{20}\left\{\begin{matrix}H^{11}\\NO^4\end{matrix}\right\}$	(prepared)
Paranicine	$C^{20}H^{13}N$	(prepared).

Journ. für Prakt. Chem., lv. p. 66.

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ANALYTICAL CHEMISTRY.

On a new Method of determining Nitrogen. *By* M. HEINTZ.

THE method proposed by the author is a further development of that of Dumas, Delbrück, and Gottlieb. According to it the substance is burnt with oxide of copper after the combustion-tube has been rendered free from air by filling with hydrogen, and subsequent heating of that part of the oxide of copper which is not mixed with the substance to be analysed. Since the combustion of nitrogenous, and especially animal substances, is frequently in the highest degree imperfect when effected by means of oxide of copper alone, and thus a part of the nitrogen may escape observation, there is introduced into the tube, between the bicarbonate of soda in the drawn-out point of the tube and the oxide of copper, a layer of chlorate of potash, the oxygen of which very nearly suffices to convert the quantity of substance employed into carbonic acid, water and nitrogen. The requisite amount may be approximatively calculated with ease when the quantities of carbon and hydrogen have been previously determined.

After the combustion is completed, oxygen is gradually liberated from the chlorate of potash, and its complete absorption by the metallic copper effected by setting free carbonic acid from the bicarbonate, at first very gradually, by which it is slowly driven into the region of the ignited copper. Finally, by more rapid heating of the salt, the nitrogen is driven into the graduated glass, which is filled partly with caustic potash and partly with quicksilver.

But the most essential part of the new method consists in the correction which is given for that error, which arises from the circumstance that the air cannot be completely driven out of the tube either before or after the combustion. For instance, after the hydrogen has been passed through the apparatus, and the point of the combustion-tube sealed at the place where the bicarbonate of soda is placed, the oxide of copper is heated. Water is formed, and the mercury rises in the evolution-tube; but it could not rise to the height of the barometer because there is water in the tube. In order to remove this, a layer of fused caustic potash, at least 4 inches long, is introduced into that end of the combustion-tube nearest to the delivery-tube. By this means the water and the small quantity of carbonic acid evolved during the sealing of the tube are completely absorbed, and the height of the mercury gives, with the aid of the barometer-height, the pressure to which the gases in the tube are exposed. It may easily be imagined that the height of the former is within a quarter of an inch less than the barometer. During the combustion, the carbonic acid and water are gradually absorbed by the caustic potash, the former however only at first in consequence of the formation of a crust of carbonate.

After the combustion is completed, the nitrogen can be easily driven out by the carbonic acid evolved from the bicarbonate.

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When this has been effected, the caustic potash absorbs, slowly indeed, but completely, the whole of the carbonic acid and water in the tube. If now the height of the mercury in the delivery-tube has been marked off before the combustion by two small brass clamps, one of them furnished with a steel point which accurately touches the surface of the mercury in the trough, the other indicating the highest point of the mercury in the delivery-tube, it is easy to measure the difference in the heights of the mercury before and after the combustion. By means of the formula

$$x = \frac{a}{760}(b - B - [q - Q]),$$

in which x signifies the difference between the quantities of oxygen remaining in the apparatus with a pressure of 760 millims., B and b the heights of the barometer before and after the combustion, Q and q the height of the column of mercury in the delivery-tube before and after the combustion, and a the volume of gas contained in the combustion-tube; then x, which must be added to or subtracted from the directly measured volume of nitrogen according as it has a positive or negative value, may be easily calculated when the value of a is known.

Heintz proposes to determine this value in the following manner:—The combustion-tube is weighed before it is filled; the quantity of quicksilver which it will contain is also weighed, and finally the filled tube. By dividing the weight of this metal by 13·6, the specific gravity of mercury, there is obtained the volume of the empty tube in cubic centimetres, and through division of the weight of the filled tube by the specific gravity of oxide of copper, 6·4, which Heintz at first considered as the mean specific gravity of the material introduced into the tube, there is obtained the volume of the contents in cubic centimetres. By the difference of these two volumes is found the volume of gas for which there is still space in the tube when charged. However, the number 6·4 for the specific gravity of the charging is not correct. According to a somewhat approximative determination, Heintz found it about 5, and it is therefore better to employ this number in preference to the former. The differences which this correction would show if this or the other number is adopted have however such a slight influence upon the final result when the experiment is well conducted, that they would not in any case affect the second decimal place. The experiments which Heintz has instituted for the purpose of testing this method prove its worth by their results. In uric acid he found, instead of 33·33 per cent. nitrogen which calculation requires, 33·40, 33·36 and 33·38 per cent., and in hippuric acid, instead of 7·82 per cent., 8·01 and 7·76 per cent.—*Bericht der Acad. der Wissensch. zu Berlin*, 1851, pp. 753–756.

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THE CHEMICAL GAZETTE.

No. CCXXVIII.—April 15, 1852.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Œnanthic Æther and Œnanthic Acid. By W. Delffs.

This rare member of the æther family, first investigated by Liebig and Pelouze* in 1836, and shortly afterwards by Mulder†, has recently been the subject of an examination by the author. The first two chemists ascribe to this æther the formula $C^{18} H^{18} O^3 = C^4 H^5 O + C^{14} H^{13} O^2$, and in the calculation of their analyses rely especially upon a determination of the density of the vapour. They found this 10·508, with which the calculation corresponded very closely, under the assumption that the constituents of the above formula were condensed to *two* volumes.

Since however organic compounds generally, and the æthers especially, are now considered as being condensed to 4 vols., this anomaly is calculated to excite a doubt as to the correctness of that determination, the more so as the vapour of a body of purely organic origin seldom reaches so high a specific gravity as is indicated by the above number. The author considers that there may have been an error in the calculation, and is strengthened in this opinion by the uncommon capacity of saturation which is presented in the lead and silver salts of the œnanthic acid, if the formula $C^{14} H^{13} O^2$ deduced from the analysis is considered to be the true one. In this case it would be necessary to assume that 2 equivs. of these bases are respectively combined with 3 equivs. of the acid. Moreover, there is scarcely any organic acid, much less fatty acid, which contains *two* equivalents of oxygen. The author also points out that the relation between the composition and boiling-points of organic compounds indicates that the composition of œnanthic æther must have another expression than that of Liebig and Pelouze. Led to the examination of this body by these considerations, he obtained the following results:—

1. *Œnanthic Æther.*—The substance employed had a yellowish colour and a feeble acid reaction. It was submitted to a fractional distillation. Ebullition commenced when the immersed thermometer stood at 464° F. The temperature then rose rapidly to 474°·8 F., and here began to be stationary. The receiver was then changed, and the distillation continued for two hours without the

* Pogg. Ann. xli. p. 571; also Ann. der Pharm., xix. p. 241, and Ann. de Chim. et de Phys., lxiii. 113.

† Pogg. Ann., lxi. p. 582.

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thermometer rising above 482° F. The liquid which passed over during this interval, amounting to nearly the fourth part of the raw æther, was used in the following experiments. It was perfectly colourless, but still showed a feeble acid reaction; it was therefore washed with a solution of carbonate of soda, dried by chloride of calcium, and rectified.

When the æther thus purified was used for a determination of the boiling-point, it again acquired a yellowish tinge, and presented an entirely peculiar phænomenon during ebullition over a spirit-lamp, with or without platinum wire. Bubbles of vapour burst from the liquid from time to time with a noise as if the retort had cracked, and each time forming a cloud of vesicles. Singularly enough, no signs of this action were shown when the æther was heated upon a sand-bath. It differed from the well-known sudden agitation which many liquids present in boiling, by not causing any perceptible disturbance in the quiet progress of the ebullition. After the æther had been a second time rectified, when a yellowish residue again remained, this phænomenon was presented but in a very slight degree, though the boiling-point differed from the former by scarcely half a degree.

The æther thus purified was colourless, had a pleasant vinous odour, and a taste at first slight, afterwards acrid; spec. grav. 0·8725 at 60° F.; index of refraction 1·4144 at 56°·3 F.; boiling-point very constant at 439° F., under a pressure of 27″ 8‴·1, and the mercury at a temperature of 57°·2 F. The analysis of the æther with oxide of copper gave the following results:—

Carbon	70·6	70·5	22 =	132	70·97
Hydrogen	11·8	11·8	22	22	11·83
Oxygen	17·6	17·7	4	32	17·20

These analyses agree sufficiently well with those of Liebig and Pelouze when their results are calculated according to C=6, H=1, O=8. The grounds for the calculation of the formula follow afterwards.

A determination of the density of the vapour was next made for the control of the equivalent. The results were—

Weight of the flask filled with air....	23·795 grms.
Height of the barometer	27″ 10‴·8
Temperature	55°·4 F.
Weight of the flask filled with vapour..	24·531 grms
Height of barometer	27″ 11‴·2
Temperature of the oil-bath	518° F.
Volume of the flask	215 cub. centims.
Volume of the residual air.....	0

The specific gravity resulting from these data is 7·042. On the contrary, the formula $C^{22} H^{44} O$ requires—

22 vols. Carbon	18·3084
44 vols. Hydrogen	3·0514
4 vols. Oxygen	4·4384
	25·7982

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Calculated spec. grav. $\frac{25{\cdot}7982}{4} = 6{\cdot}449.$

The difference between experiment and calculation is indeed greater than is desirable; but when it is remembered that the experiment always gives too high a number when the determination of the density does not take place at a temperature sufficiently remote from the boiling-point, this difference appears less important than at the first glance. To ensure accuracy in these experiments, the temperature at which the flask is sealed should be in round numbers 181° F. higher than the boiling-point of the liquid. However, as œnanthic æther boils at 435°·2 F., the temperature would have to be raised to 616° F., which, besides the danger of inflaming the oil, appears to be too high for organic bodies. In the present instance the author considered it unnecessary to repeat the determination at a higher temperature, as the æther in the flask had already assumed a slight yellow colour; but whatever doubt the density of the vapour may leave with regard to the correctness of the equivalent deduced, he considers is removed by his experiments with the œnanthic acid.

2. *Œnanthic Acid.*—The œnanthic æther readily decomposes when warmed with caustic potash. Hydrochloric acid afterwards added in excess separates the acid in the form of a slightly yellowish oil, which solidifies on cooling to a snow-white mass, showing scarcely any traces of crystallization. It dissolves in alcohol, even in the cold, with great readiness, and almost in every proportion in æther. It separates from the former solution on spontaneous evaporation as a crystalline mass. When pure, it is perfectly destitute of odour and taste, and melts even with the heat of the hand. The accurate determination of the melting-point is attended with difficulties, as it passes into a buttery state before the actual melting; it is certainly below 77° F. The acid dissolves easily in ammonia, giving on evaporation a smeary soap, which does not again form a clear solution in water. The most neutral solution of the ammonia salt gave with nitrate of silver a white caseous precipitate, not perceptibly soluble in boiling water. The washed precipitate was first dried in a dark room upon a small water-bath, and retained its white colour; but after it had been heated for some time in a close water-bath, it assumed a straw-yellow colour, and at the same time a pulverulent appearance. In the following silver determinations, the white salt was used in the first, and the yellow in the two others:—

I. gave 39·5 per cent. of metallic silver.
II. gave 40·4 per cent. of metallic silver.
III. gave 40·5 per cent. of metallic silver.

Probably the white salt still contained some water mechanically mixed, and moreover the first experiment was not conducted so cautiously as the last two. In consequence of the pulverulent character, the temperature must be raised with extreme slowness. The author therefore disregards the first determination, and fixes the equivalent of the anhydrous acid at 150–151 from the latter two.

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In consequence of the difficulty in burning fatty acids, and the smeary character of this body, he preferred employing the silver salt for analysis, the results of which were:—

Carbon	41·0	18 =	108	40·75
Hydrogen	6·5	17	17	6·42
Oxygen	12·0	4	32	12·08
Silver	40·5	1	108	40·75

A repetition of this analysis was considered unnecessary, as the analyses of the hydrated œnanthic acid by Liebig and Pelouze corresponded sufficiently with the formula $HO + C^{18} H^{17} O^3$ when the results obtained by them were calculated according to the later equivalents, as is evident from the following comparison:—

	Calculated.			Liebig and Pelouze.
Carbon	68·35	18 =	108	68·63
Hydrogen	11·40	18	18	11·61
Oxygen	20·25	4	32	19·76

If from the equivalent of the hydrated œnanthic acid 1 equiv. of water is deducted, there is obtained the number 140, which corresponds very closely with the equivalent deduced from the silver determination.

It follows from these results that œnanthic acid corresponds perfectly in its composition with the pelargonic acid analysed by Redtenbacher and Pless*. The characters of this acid also correspond with those given by Redtenbacher for the pelargonic. As this chemist examined the baryta salt of the latter acid as well as the silver, and as it was especially adapted to the control of the equivalent determination, that of the œnanthic acid was also analysed. Baryta-water was boiled with a slight excess of the acid, the salt freed from admixture with carbonate by solution in boiling water and filtration while hot. In the course of twenty-four hours the œnanthate separated in small lamellar crystals. The analogy with cholesterine, stated by Redtenbacher to be possessed by the pelargonate of baryta, was not observed; but Delffs considers this difference of form of little importance, as he has observed the butyrate of baryta to occur in crystals of very different character, although, in accordance with Lerch's statement, all equally anhydrous. The composition of the œnanthate of baryta, dried at 212° F., and not presenting any traces of efflorescence, corresponded perfectly with the pelargonate of baryta; for 100 parts contained—

		Found.	
	Calculated.	I.	II.
Baryta	33·78	33·84	33·89
Œnanthic acid	66·22	66·16	66·11

According to the above results, Delffs considers that there is no doubt that the œnanthic and pelargonic acids are identical, and that both must be represented by the formula $C^{18} H^{17} O^3 + HO$.

One point in reference to Liebig and Pelouze's investigation which still remains undecided, is the change which the acid is said to

* Ann. der Chem. und Pharm., lix. p. 52.

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undergo by distillation. This the author was unable to follow up from want of material, but the portions which passed over at a high temperature appeared to him to contain an acid with a higher equivalent (capric acid?).

The conversion of organic baryta salts into carbonate of baryta by simple ignition in a flat platinum dish affords a very convenient means of ascertaining the equivalent of an organic acid. The accuracy of this method is evident from the following example:—1000 parts of butyrate of baryta left 632–634 parts of carbonate of baryta, or 49·03–49·17 per cent. of pure baryta. Theory requires 49·01.—Poggendorff's *Annalen*, lxxxiv. p. 505.

On the Nitrite of Lead. *By* A. Gomès.

M. Nicklès announced some time ago the isomorphism of the nitrate of lead, and of the nitrite of the same metal crystallized with water, without however supporting his assertion either by crystallographical measurements or by complete analyses of the nitrite in question. The formation of this last salt by carbonic acid, and the yellow spangles described by M. Peligot under the name of hyponitrate of lead, and considered by M. Gerhardt as a double basic salt of the nitrate and nitrite, rendered somewhat doubtful the composition assigned to this salt as nitrite. I have therefore undertaken, in the laboratory and under the kind guidance of M. Gerhardt, some complete analyses of this compound.

According to the hypothesis of M. Nicklès, it should contain 65·4 per cent. of lead; now all my analyses made upon salts beautifully crystallized show that such is not the composition of the body, and that it contains much less lead. With respect to the amount of water, I found nearly the same quantity stated by Berzelius. With respect to the nitrogen, the proportion contained in the salt is too small to be taken into consideration in the discussion of the formulæ. Moreover, the direct estimation of the lead can alone decide the question. The following are the analyses:—

					Nicklès' formula
Lead	63·7	63·7	63·5	63·3	65·4
Nitrogen	8·3	8·5	..	..	8·8
Hydrogen	0·5	0·6	0·6	..	0·6

The only formula which agrees with these numbers is that of a double neutral salt, composed of 1 atom of nitrate of lead and of 3 atoms of nitrite, $NO^3Pb, 3NO^2Pb + 2Aq$*. This formula requires—

Lead	63·8
Nitrogen	8·5
Hydrogen	0·6

It will be observed that this substance is the neutral salt which results from the decomposition of a similar double but basic salt by carbonic acid, only that in the decomposition of the latter nitric

* Gerhardt's notation.

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acid is at the same time eliminated, for the solution becomes exceedingly acid by passing carbonic acid through it, and when left to itself over sulphuric acid constantly evolves colourless vapours of nitric acid. It is indeed this nitric acid which holds the salt in solution; for when the crystals are boiled with water, a large quantity of bibasic subnitrate of lead is formed without any disengagement of gas. The composition of this salt, which has been erroneously considered as a simple nitrite, is interesting from its being perfectly similar to that of several other compounds of nitrate of lead, as will be seen from the following formulæ:—

$NO^5 Pb, PO^4 Pb^3 + 2Aq$, double nitrate and phosphate of lead.
$NO^5 Pb, NO^2 Pb, Pb^2O + Aq$, double basic nitrate and nitrite of lead.
$NO^5 Pb, 3NO^2 Pb + 2Aq$, neutral nitrate and nitrite of lead.
$NO^5 Pb, 3PbHO$, double nitrate and hydrate (subnitrate) of lead.

It is seen that in all these salts the amount of lead contained in the nitrate is to the lead contained in the salts combined with it as 1 : 3.—*Comptes Rendus*, Feb. 2, 1852.

On some new Products of the Action of Nitric Acid upon Members of the Benzoic Series. *By* C. Bertagnini.

The results obtained in this investigation, a brief notice of which appeared in a former number of this Journal*, show that—

1. *Oil of bitter almonds*, on treatment with nitrosulphuric acid, exchanges 1 equiv. hydrogen for 1 equiv. NO^4.

2. Nitrated oil of bitter almonds furnishes a further series of nitrated derivatives perfectly parallel with those of the original oil.

3. These derivatives have the greatest analogy with those corresponding bodies in the original series.

The author treated the oil of bitter almonds, which is converted, as is well known, into benzoic acid by ordinary nitric acid, with fuming nitric acid, or instead of this a mixture of 1 vol. nitric acid of 1·32 spec. grav. with 2 vols. of commercial sulphuric acid. 1 part of oil of bitter almonds is poured into from 15–20 parts of this mixture, which is well cooled, otherwise nitrobenzoic acid is obtained. On adding water, an oily substance falls in little globules, which subsequently solidify. They are collected upon linen, washed, and dried between two porous tiles, which removes a yellowish oily substance of a peculiar garlic odour, which prevented the crystallization of the principal substance. The oily yellowish substance is sufficiently removed when the crystalline mass is no longer of a yellow colour. It is now dissolved in a little boiling alcohol, from which it separates on cooling in the form of an oil, but subsequently congeals to a crystalline mass; from the mother-liquor it separates directly in the crystalline form. The substance may also be dissolved in hot water, but dilute alcohol is preferable.

Nitrated Oil of Bitter Almonds, $C^{14} H^5 (NO^4) O^2$, dissolves very sparingly in cold water, readily in alcohol and æther. It dis-

* Chem. Gaz. vol. ix. p. 213.

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solves without alteration in nitric, hydrochloric and sulphuric acids. The sulphuric acid solution deposits it in crystals in proportion as this absorbs moisture from the atmosphere. It has a pungent taste, resembling oil of bitter almonds; it smells but very slightly in the air. It melts readily, and then diffuses an agreeable odour, but which, as the temperature increases, becomes disagreeably pungent. The melted oil solidifies at 115°–120° F. It sublimes unaltered. Large masses become coated on the surface with a crystalline bloom after long preservation. Analysis gave—

Carbon.....	55·54	56·02	55·72	14	55·62
Hydrogen.....	3·43	3·63	3·40	5	3·31
Nitrogen	9·42	9·42	9·42	1	9·27
Oxygen.....	31·61	31·83	31·46	6	31·80

The nitrated oil of bitter almonds stands in the same relation to nitrobenzoic acid as oil of bitter almonds to benzoic acid:—

Oil of bitter almonds..... $C^{14}H^6O^2 + O^2 = C^{14}H^6O^4$.
Nitrated oil of bitter almonds, $C^{14}H^5(NO^4)O^2 + O^2 = C^{14}H^5(NO^4)O^4$.

This oxidation into nitrobenzoic acid is effected by oxidizing agents, and also by the mere action of potash and access of air. The oxidation does not proceed so rapidly as that of the oil of bitter almonds; it succeeds by treating the oil with concentrated chromic acid. It is most easily effected by potash dissolved in alcohol.

Perchloride of Nitrobenzoyle, $C^{14}H^4Cl(NO^4)O^2$, is produced when the hydruret of nitrobenzoyle is treated in direct light with chlorine: it forms a yellowish liquid. Bromine has no action at a low temperature, but appears to have the same effect as chlorine at higher temperatures.

Nitrosulphuret of Benzoyle, $C^{14}H^5(NO^4)S^2$, is produced by treating an alcoholic solution of nitrobenzoyle with sulphuretted hydrogen.

Trinitrobenzamide, $C^{12}H^{15}(NO^4)N$, is formed by ammonia from the hydruret of nitrobenzoyle in the same manner as hydrobenzamide from oil of bitter almonds. This passes by mere molecular change into trinitramarine.

Concentrated prussic acid dissolves it, and deposits the dissolved product after some time in crystals with all its properties; but after the lapse of several hours, and on evaporation, these crystals are no longer obtained, but in their stead a viscous liquid, which is unalterable in the air and soluble in hot water, from which it separates in oily drops.

When this product is boiled with hydrochloric acid, chloride of ammonium and another substance soluble in water are obtained. Cyanide of potassium immediately converts the hydruret of nitrobenzoyle into a different substance.

Urea forms with the hydruret of nitrobenzoyle a peculiar substance, which is probably analogous with that prepared by Laurent and Gerhardt from oil of bitter almonds. To prepare it, urea is thrown upon melted hydruret of nitrobenzoyle and gently heated; an opake mass is obtained, which solidifies on cooling. In pure

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alcohol it is sparingly soluble, but it dissolves entirely in alcohol which has been acidified with hydrochloric acid, and is then resolved into its components.

Sulphuret of Ammonium and Hydruret of Benzoyle.—The hydruret of nitrobenzoyle is dissolved in ammoniacal alcohol, a current of sulphuretted hydrogen passed into it, and heat applied from time to time. A semi-fluid substance, mixed with much sulphur, collects at the bottom of the vessel; the supernatant alcoholic solution is decanted, and the residue dissolved in æther. The æther leaves on evaporation a sulphurous substance, which is insoluble in water and in water acidified with hydrochloric acid, but soluble in alcohol. On ebullition with nitric acid, sulphuric acid is generated. Heated in a tube, the substance puffs up, and gives off sulphuretted hydrogen.

Chlorine and Hydruret of Nitrobenzoyle.—Dry chlorine does not act in diffused light, whilst in direct sunlight it converts the substance into a very mobile liquid, which can easily be distilled. This is heavier than water, and insoluble in water. By long contact with water, it passes into nitrobenzoic acid. Potash yields the same product, ammonia and nitrobenzamide. Lastly, it has all the properties which Cahours has ascribed to the product obtained by the action of perchloride of phosphorus upon nitrobenzoic acid. It is therefore—

The Perchloride of Nitrobenzoyle, $C^{14} H^4 Cl (NO^4) O^2$.—It has nearly the odour of perchloride of benzoyle, and the same tendency to part with its chlorine to other substances. It is therefore especially adapted for obtaining substances which belong to the series of the nitrobenzoic acid, in the same manner as the perchloride of benzoyle serves for the preparation of the members of the benzoic acid series.

Ammonia, both the gas and the solution, forms solid nitrobenzamide with it. It dissolves in alcohol, and produces hydrochloric acid and the æther of nitrobenzoic acid, which is obtained in very beautiful crystals on evaporating the liquid. Methylic alcohol likewise dissolves it, and produces the methylic æther, which crystallizes. Aniline is decomposed by it, with evolution of much hydrochloric acid, into nitrobenzanilide, which dissolves in alcohol and crystallizes in needles. Of all the solvents tried, anhydrous æther was the only one which exercised no decomposing action on the hydruret of nitrobenzoyle.

Sulphuretted Hydrogen and Hydruret of Nitrobenzoyle.—When a current of sulphuretted hydrogen is passed into the solution of the hydruret of the nitrobenzoyle in alcohol, in the course of some time bisulphated hydruret of the nitrobenzoyle is deposited in the form of a white powder. The product is nitrobenzoyle, in which the 2 atoms of oxygen have been exchanged for sulphur, $C^{14} H^5 (NO^4) O^2 + 2HS = C^{14} H^5 (NO^4) S^2 + 2HO$. This new substance forms a grayish powder, which on being rubbed between the fingers diffuses a disagreeable odour. It becomes electric by friction, is insoluble in the most ordinary solvents, melts in boiling water, and forms

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opake drops; the aqueous vapour which is given off has an odour of garlic. In alcohol it forms an adhesive mass; in æther it becomes semi-fluid and viscous; sulphuric acid dissolves it at a gentle heat without turning black; the solution is precipitated by water. Ordinary nitric acid oxidizes the whole of the sulphur into sulphuric acid, and separates unaltered nitruret of benzoyle, or converts it into nitrobenzoic acid. It deserves attention that the new sulphated compound gives off its sulphur as sulphuretted hydrogen when exposed at the ordinary temperature to a current of gaseous ammonia. The hydruret of nitrobenzoyle now loses in contact with ammonia its oxygen, and forms trinitrobenzamide. There can scarcely be a doubt therefore that the substance remaining after treatment of the sulphated compound is trinitrobenzamide. Analysis gave—

Carbon	49·80	50·11	14	50·29
Hydrogen	3·30	3·45	5	2·99
Nitrogen	8·74	8·27	1	8·38
Sulphur.....	19·22	18·67	2	19·18
Oxygen	..	..	4	19·16

Ammonia and Hydruret of Nitrobenzoyle.—In all cases where ammonia, either dry or dissolved in water or alcohol, comes into contact with nitrated oil of bitter almonds, trinitrobenzamide is formed. When ammonia is poured over the nitrated oil of bitter almonds in the state of powder, it is gradually converted into a resinous mass. The reaction is complete in the course of a day; trinitrobenzamide is formed without any collateral products, according to the equation $3C^{14}H^{5}(NO^{4})O^{2}+2NH^{3}=C^{42}H^{15}(NO^{4})^{3}N^{2}+6HO$.

This substance, prepared by the above method, may easily be purified by digestion or washing with cold dilute alcohol, when it forms a light white powder without the least trace of crystallization; it can however be obtained in crystals by solution in hot alcohol. It is insoluble in water, æther and oil of turpentine. Strong boiling alcohol dissolves it in small quantity, and leaves it on cooling in microscopic shining needles, which are deposited in flakes. It is inodorous and tasteless. On being boiled for some time with alcohol, it is again resolved into nitrated oil of bitter almonds. When a little hydrochloric acid is added to the alcoholic solution, the decomposition is almost instantaneous. It dissolves readily in a concentrated solution of chromic acid; the solution contains nitrobenzoic acid.

Trinitramarine, $C^{42}H^{15}N^{5}O^{12}$.—When trinitrobenzamide is heated with a dilute solution of caustic potash (1 vol. of ley at 46° Beaumé and 50 vols. water), a brown semi-fluid mass first forms, which subsequently becomes hard. The brown mass is dissolved in strong alcohol with which a little æther has been mixed, and muriatic acid added, when the hydrochlorate of trinitramarine separates almost immediately in small crystals, whilst the impurities remain in solution. They are purified by treatment with weak alcohol, decomposed by an alcoholic solution of ammonia, the solution con-

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taining the new alkaloid evaporated, and the residue washed with water until it no longer contains any more chloride of ammonium. It may be obtained in a more simple manner by heating trinitrobenzamide in an oil-bath to 257°–302°; a resinous mass first forms, which subsequently becomes hard and brittle. As evident from what precedes, the new base is isomeric with trinitrobenzamide. The author has as yet only determined the amount of nitrogen; he found 16·05; theory requires 16·16. It becomes nearly liquid in boiling water, in which it is sparingly soluble; the solution is alkaline. It dissolves in boiling alcohol, from which it separates on cooling in the amorphous state; it is readily soluble in æther, and in a mixture of æther and alcohol. The solutions have a bitter taste. It forms double salts with chloride of platinum and perchloride of mercury, and gives with nitric acid a salt which is insoluble in water, readily soluble in alcohol, from which it separates in needles.

The Hydrochlorate, $C^{42}H^{15}N^{5}O^{12}$, HCl, is more sparingly soluble than the preceding; it therefore separates on cooling when the boiling alcoholic solution of the base is mixed with hydrochloric acid in shining needles; boiling alcohol dissolves some of the salt. The author obtained 15·03 nitrogen and 7·11 chlorine; theory requires 14·90 and 7·56.

Trinitramarine is the only one among the alkaloids which appears capable of exchanging 3 equivs. hydrogen for 3 equivs. of hyponitric acid, and so to comprise the very complex group of atoms with $N^{3}O^{12}$. The process followed in the present case for the metamorphosis of the trinitramarine by treatment at a high temperature appears to show that other hydramides may be converted into bases in the same way. Furfurine and amarine have been obtained by treatment of their hydramides; it is probable therefore that furfuramide and benzamide may also be converted at an elevated temperature into furfurine and amarine, as would be expected from the similarity of furfuramide, hydrobenzamide and trinitrobenzamide. The compounds prepared by the author exhibit in their composition the following parallelism:—

$C^{14}H^{6}O^{2}$, oil of bitter almonds.	$C^{14}H^{5}(NO^{4})O^{2}$, hydruret of nitrobenzoyle.
$C^{14}H^{5}ClO^{2}$, chloride of benzoyle.	$C^{14}H^{4}(Cl,NO^{4})O^{2}$, hydruret of chloronitrobenzoyle.
$C^{14}H^{6}S^{2}$, sulphated oil of bitter almonds.	$C^{14}H^{5}(NO^{4})S^{2}$, sulphated nitro-compound.
$C^{14}H^{6}O^{4}$, benzoic acid.	$C^{14}H^{5}(NO^{4})O^{4}$, nitrobenzoic acid.
$C^{42}H^{18}N^{2}$, hydrobenzamide.	$C^{42}H^{15}(NO^{4})^{3}N^{2}$, trinitrobenzamide.
$C^{42}H^{18}N^{2}$, amarine.	$C^{42}H^{15}(NO^{4})^{3}N^{2}$, trinitramarine.

Ann. de Chim., vol. xxxiii. p. 465.

On a new Acid extracted from the Mother-Liquors of the Fulminate of Mercury. *By* S. Cloez.

The action of nitric acid upon alcohol in the presence of nitrate of mercury or of nitrate of silver, furnishes some peculiar salts,

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which have long been known by the name of *fulminates*. The salt of mercury discovered by Howard, which is prepared at the present time in such large quantity for the manufacture of percussion caps, offers a certain interest, there being considerable room for œconomy in its preparation.

The reaction which gives rise to the fulminate produces at the same time a large number of neutral or acid substances, which remain in solution in the mother-liquors and in volatile liquids which are condensed. The acid mother-liquors are of no value to the manufacturer; in seeking to turn some of the substances which they contain to account, I discovered the acid which forms the subject of the present notice.

To extract this acid, the mother-liquors are neutralized with chalk, the solution filtered to separate the excess of carbonate in suspension, and the clear liquid distilled in a water-bath. The product contains aldehyde and nitric, formic and acetic æthers; a black liquid, of a syrupy consistence and the odour of caramel, remains in the retort. This liquid has a very complex composition; it contains a large amount of nitrate and formiate of lime, a little acetate of the same base, and a certain quantity of the salt of lime of the new acid. On leaving this liquid to spontaneous evaporation, a crystalline mass of lime-salts is obtained; the nitrate of lime, which remains dissolved, is separated by decantation; and in order to remove every trace, the crystalline mass is washed with alcohol of 0·836. The acetate and formiate of lime are removed by dissolving the crystals in water, and adding to the liquid oxalic acid only in sufficient quantity to precipitate the whole of the lime; after filtering, the liquid is heated in a retort to separate the formic and acetic acids. A strongly acid, brownish, syrupy liquid is left, which is decolorized with animal charcoal; on combining this acid again with lime, a white salt is obtained, which is purified by repeated crystallization.

The pure salt, at the moment when it separates from the aqueous solution, resembles the lactate of lime; like the latter, it forms light mammillated agglomerations, but it is easily distinguished by its perfect insolubility in boiling alcohol.

On treating a solution of the pure lime-salt with a solution of oxalic acid, a colourless acid is obtained, which is concentrated at first on the water-bath, and subsequently *in vacuo* over sulphuric acid. At its maximum of concentration, it forms a syrupy liquid, similar to lactic acid; its composition is represented by the formula $C^4 H^4 O^6 = C^4 H^3 O^5, HO$; it is homologous with lactic acid, $C^6 H^6 O^6 = C^6 H^5 O^5, HO$, for which reason I have given it the name of *homolactic acid*. The series of these acids, should it be further extended, might be represented in a general manner by the formula $C^{2n} H^{2n} O^6 = C^{2n} H^{2n-1} O^5, HO$. Homolactic acid is a syrupy, colourless, inodorous liquid; its specific gravity at 55° is 1·197; it absorbs moisture from the atmosphere, dissolves entirely in alcohol and æther, has an acid taste, coagulates milk, and dissolves iron and zinc with disengagement of hydrogen. When heated in a closed tube or in a retort above 392°, it is decomposed, giving off white

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fumes, which condense into a solid white substance, but which I could not obtain in sufficient quantity to determine the composition: a carbonaceous residue is left at the bottom of the tube.

Homolactic acid forms perfectly-defined salts with most of the bases; the homolactate of silver crystallizes in long, thin, colourless plates, which are sparingly soluble in cold water. The salt is anhydrous, and its composition may be represented by the formula $C^6 H^5 O^5$, AgO.—*Comptes Rendus*, March 8, 1852.

On the Absorption of the Soluble Salts of Ulmic Acid by Plants. By J. Malaguti.

Soubeiran concluded, from two experiments which he had made on the absorption of the ulmate of ammonia, that this salt was taken up by plants. In one experiment, a plant was placed with its roots in a solution of ulmate of ammonia; it continued to grow in it, and the solution became partially decolorized. In the second experiment, beans and oats were found to succeed perfectly well in a soil which had been deprived of organic matter, but which contained some sulphate and phosphate of lime, and was watered with a solution of ulmate of ammonia.

The author's object was to check Soubeiran's experiments by the balance. He filled two large funnels half-full with gravel and the other half with pounded brick, which contained one-hundredth of calcined bone and the same amount of chalk. The same quantity of cress-seed was sown in each. As soon as they began to germinate, a perfectly neutral solution of ulmate of ammonia was prepared from peat; the solution (2 litres) was divided into two equal parts; one was kept, the other used to water the soil in one of the funnels.

Four days after the seeds were sown, they were watered daily with 100 cub. centims. of water, the others with the solution of ulmate of ammonia. Already on the fifth day there was a perceptible difference in the appearance of the plants; those moistened with water only were light green, the others dark green.

Eighteen days after the watering, or on the twenty-second day of the experiment, the plants were collected entire with the roots. Those which had been watered with the solution of ulmate of ammonia weighed 15·150 grms., the others 12·550 grms.

The author now exhausted the soil which had been watered with ulmate of ammonia alternately with hydrochloric acid and ammonia, made the extract neutral, precipitated with chloride of calcium, and weighed the precipitate. The 1 litre of ulmate of ammonia, which had been preserved for comparison, was precipitated with chloride of calcium; it gave 5·7 grms. precipitate, whilst the first, which must have originally contained the same quantity, furnished only 3·1 grms. The difference of 2·6 grms. has therefore been absorbed by the plants.

The ulmate of lime furnished, on the analysis of 0·590 substance, 0·053 lime, according to which the ulmate of ammonia used to water

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the plants must have lost 2·367 ulmic acid. Hence the author concludes with Soubeiran, that the soluble ulmates are absorbed, and applied in the vegetation of plants.—*Comptes Rendus*, xxxiv. p. 112.

On the Compounds of Carbonic Acid and Water with Oxide of Zinc. By Prof. H. Rose.

Oxide of zinc forms with carbonic acid and water a far larger number of compounds than is produced in the precipitation of solutions of neutral salts of other oxides, as for instance magnesia, oxide of lead, copper, cobalt and nickel, by carbonated alkalies. In the case of these latter, but few compounds are formed of neutral carbonate of the oxide with a hydrate of the oxide, which owing to the affinity they exert on each other resist more or less with a certain obstinacy the further action of water; but in the precipitation of sulphate of zinc by the carbonate of soda, various compounds are formed between the carbonate of zinc and the hydrated oxide, several of which, even in drying, alter their composition, carbonic acid being expelled by the water.

From concentrated solutions of equivalents of the two salts, the compound $2ZnO, CO^2 + 3ZnO, HO + HO$ is the one which generally falls in the cold, but which on being dried is converted into $4ZnO, CO^2 + 7ZnO, HO + HO$. This also separates when more dilute solutions are mixed. From very dilute cold solutions, and likewise from boiling concentrated solutions, the precipitate obtained has generally the formula $ZnO, CO^2 + 2ZnO, HO$ combined with various amounts of water. With an excess of carbonate of soda, and according as the precipitation is effected in the cold or at an elevated temperature, the compounds procured contain somewhat more carbonic acid; but in preparing very large quantities according to the proportions prescribed by the Prussian Pharmacopœia, and using only a somewhat elevated temperature, there is apparently always obtained a precipitate having the simple composition $ZnO, CO^2 + ZnO, HO$.

When bicarbonate of soda is used for the precipitation of the sulphate of zinc, the compounds obtained are richer in carbonic acid; they must not however be placed under the air-pump to dry while in a moist condition, as much carbonic acid then escapes, $2ZnO, CO^2 + 3ZnO, HO + HO$ being formed. When the precipitation is effected in the cold with an excess of the bicarbonate, the compound has the formula $4ZnO, CO^2 + 5ZnO, HO + HO$; but when very large quantities are operated upon, the precipitate which falls even at a somewhat elevated temperature is $2ZnO, CO^2 + ZnO, HO$. When an excess of bicarbonate is used, and the precipitate (from cold solutions) let stand for some time and not washed, it contains the largest amount of carbonic acid, and has the composition $12ZnO, CO^2 + 3ZnO, HO + 5HO$. It does not part with any carbonic acid at 212°, but only with water, being converted into $4ZnO, CO^2 + ZnO, HO$.

The neutral compound of oxide of zinc with carbonic acid is only

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obtained by mixing an excess of a concentrated solution of bicarbonate of potash in the cold with one of sulphate of zinc. The precipitate is set aside for some time until it has become dense, and then washed with a solution of carbonate of potash. After pressure between blotting-paper, it has the composition $2ZnO, CO^2 + 3HO$; by washing with cold water it is not altered, and has then in the air-dried state the formula $4ZnO, CO^2 + 5HO$; at 212° it parts with no carbonic acid nor with the whole quantity of water, but becomes $4ZnO, CO^2 + HO$. It is very remarkable, that even when exposed to a temperature of 392° F., no carbonic acid is expelled, and not all the water; its composition is then $5ZnO, CO^2 + HO$.

The compounds of carbonate of zinc with hydrated oxide of zinc do not hold their carbonic acid so firmly combined. At 392° they lose the whole of their carbonic acid and water, and leave pure oxide of zinc. In this case the carbonic acid is expelled by the water, which then escapes itself at 392°.

The native carbonate behaves precisely like the artificially-prepared neutral carbonate at an elevated temperature. It retains its carbonic acid at 392°, but slowly parts with it at 572°.

Whilst however a temperature of 572° is required to expel the carbonic acid from the neutral carbonate of zinc, water expels it from the pulverized mineral at 212°.—*Proc. Berlin Academy*, Jan. 15, 1852.

On the decolorizing Property of Charcoal and several other Bodies. By E. FILHOL.

It is generally stated that charcoal is the only simple body which possesses the property of absorbing colouring matter dissolved in a liquid; it further appears from the investigations of MM. Bussy and Payen, that decoloration by charcoal is a purely physical phænomenon.

Several compound bodies (alumina, sulphate of lead prepared by the moist way, hydrate of lead) also partake of the property of decolorizing liquids; but it is generally considered by chemists that the action exerted by oxides on colouring matter in the preparation of lakes, is chemical, differing in this respect from that of charcoal; nevertheless Berzelius was of opinion that the decoloration effected by the oxides and metallic salts resembled that produced by charcoal. My object has been to prove,—

1. That charcoal is not the only simple body possessing the property of decolorizing liquids; sulphur, arsenic and iron obtained by the reduction of the hydrated sesquioxide by hydrogen, are all possessed of decolorizing power.

2. That the number of compound bodies having an appreciable decolorizing power are more numerous than has been thought, and that this power appears to depend much more on the state of division of these bodies than on their chemical properties.

3. That such bodies which easily appropriate one colouring matter may have but little tendency to do so with another; thus phosphate of lime from bones (artificially obtained) scarcely decolorizes the

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sulphindigotate of soda, whilst it exercises a more energetic influence on tincture of litmus than does animal charcoal.

4. That the decoloration, in the majority of cases, is a purely physical phænomenon; thus the same colouring matter is absorbed by metalloids, metals, acids, bases, salts and organic substances. It is easy, moreover, by employing suitable solvents, to remove the colouring matter in an unaltered state from the body which had absorbed it.

I do not doubt but that these facts may prove useful in analytical chemistry and in some manufacturing processes.

The following results, which I have extracted from my memoir, will give some idea of the energy with which certain decolorizing matters act. My observations were made with one of Collardeau's double lunette colorimeters:—

Decolorizing Power of different Substances, compared to that of purified Animal Charcoal, supposed equal to 100.

	Tincture of litmus.	Sulphindigotate of soda.
Charcoal	100·00	100·00
Pure hydrate of iron	128·90	1·97
Alumina	116·00	9·91
Phosphate of lime	109·00	1·97
Iron reduced by hydrogen	95·33	100·00
Milk of sulphur	26·67	0·00
Deutoxide of manganese (native)	88·90	13·80
Indigo	80·00	13·50
Oxide of zinc	80·00	6·55
Stannic acid	70·40	0·00
Antimonic acid	66·66	1·97
Chromate of lead	70·40	2·92
Litharge	66·66	3·85
Sulphuret of antimony (native)	59·25	0·00
Sulphate of lead	50·00	13·80
Deutoxide of copper	26·67	0·00
Protochloride of mercury	22·22	0·00
Sulphate of baryta (artificial)	50·00	0·00
Sulphuret of lead (artificial)	130·00	16·67

Comptes Rendus, Feb. 16, 1852.

Observations on the Formation of Sulphuric Acid from Sulphurous Acid and Oxygen. By Prof. Wöhler.

It is well known, from the experiments of Dœbereiner and other chemists, that several metallic oxides are capable, like platinum, of supporting the slow combustion of alcoholic vapour. I considered it highly probable that this action would likewise extend to a mixture of sulphurous acid gas and oxygen, and requested M. Mahla to make some experiments on the subject in such manner that a dry mixture of about 2 vols. sulphurous acid and 1 vol. oxygen or of atmospheric air were passed over oxide heated in a glass tube to a faint red.

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1. *Oxide of Copper, Peroxide of Iron, Oxide of Chromium*, each separately employed, instantly cause the production of dense white fumes of sulphuric acid. A mixture of oxide of copper and oxide of chrome, prepared by precipitation, had in particular a very powerful action. The same amount of oxide appears capable of converting an unlimited quantity of the gases into sulphuric acid. The formation of sulphuric acid proceeds so readily, and to such an extent, that this process will undoubtedly come to be practically employed.

2. *Oxide of Copper and Oxide of Iron*, heated in sulphurous acid without oxygen, are reduced, the first to red protoxide, the latter to black protoperoxide, with production of vapours of sulphuric acid, but which however cease to appear as soon as the reduction is complete.

3. *Oxide of Chromium*, heated without oxygen in sulphurous acid, remains unaltered; not a trace of sulphuric acid is formed.

4. *Metallic Copper*, placed in a spongy state over mercury in a mixture of 2 vols. sulphurous acid and 1 vol. oxygen, exerts at the ordinary temperature, even in the course of several days, no action upon the mixture of gases. But if the spongy copper be heated in it, fumes of sulphuric acid are formed, but not before the copper has become converted on the surface into oxide.

5. *Caustic Lime*, heated in the gaseous mixture, becomes brightly incandescent, and is converted into sulphate without any formation of free sulphuric acid.

6. *Aqueous Vapour*, passed with the gaseous mixture through a porcelain tube at a faint red heat, does not induce the production of the hydrate of sulphuric acid.

7. *Platinum Foil*, polished and cleansed by treatment with hot sulphuric acid, alkali and water, acts upon the dry gaseous mixture like spongy platinum; far below red heat, it causes with great readiness the formation of anhydrous sulphuric acid, without the slightest evident alteration at its surface. It does not act at the ordinary temperature.

M. Mahla has found on this occasion that a mixture of peroxide of iron and oxide of copper, prepared by precipitation, and calcined when heated in a jet of hydrogen, becomes red-hot like spongy platinum, and remains incandescent.—Liebig's *Annalen*, Feb. 1852.

On the Constitution of Tannic Acid. By Dr. A. Strecker.

I have found that tannic acid is a conjugate sugar compound, or that it contains a carbohydrate as proximate constituent which is capable of being converted into sugar. The common experience, that even with the most careful heating of tannic acid there is always obtained a very considerable carbonaceous residue (whilst, according to the formulæ hitherto proposed, only pyrogallic and carbonic acid should occur), as well as the production of humous substances by the action of powerful acids, or in the spontaneous decomposition of this acid, have led me to the view that tannic acid contains a carbohydrate associated with gallic acid. In order to ascertain this, I con-

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verted tannic acid, prepared by extracting galls with æther by boiling with dilute sulphuric acid, into gallic acid. The solution was first precipitated with carbonate of lead, and then with neutral acetate of lead; and after removing the lead in solution by sulphuretted hydrogen, I obtained on evaporation a residue, which proved to be sugar. It possessed, in fact, a *slightly* sweet taste, and gave with sulphate of copper and potash a separation of hydrated protoxide of copper even in the cold, much more quickly on the application of a gentle heat. Having since found that the reduction of oxide of copper is effected by gallic acid, I assured myself of the absence of gallic acid by a solution of protoperoxide of iron. Mixed with yeast, a lively fermentation quickly sets in, thus still further proving the presence of sugar. To prevent the possibility of my tannic acid containing sugar, I precipitated the aqueous solution of the tannic acid with sulphuric acid, washed the precipitate with water containing sulphuric acid, and then converted it into gallic acid by ebullition with water. In this case I likewise obtained a considerable amount of sugar, which consequently must have originated from the tannic acid. It will hereafter be possible to fix the formula for tannic acid, which in my opinion it is scarcely possible to do from an analysis of the salts on account of the great variety of the compounds. I shall endeavour to determine the quantity of sugar; in the meantime I am of opinion that the formula $C^{48}H^{18}O^{26}$ may be admitted with tolerable certainty. As the statements respecting the amount of water of tannic acid differ considerably, I have prepared as pure tannic acid as possible, and burnt it in a current of oxygen. The agreement of my formula with the analyses will be seen from the following:—

	Liebig.	Berzelius.	Mulder.	Strecker.	Calculated.
Carbon.....	51·5	51·5	51·5 to 52·1	51·4 to 51·5	40=51·5
Hydrogen....	4·1	3·8	3·6 3·9	3·9 3·9	18 3·8
Oxygen	..	..	.. ..	.. ..	26 44·7

The decomposition of tannic acid into gallic acid and sugar takes place according to the equation—

$$C^{40}H^{18}O^{26}+10HO=2(C^{14}H^{8}O^{12})+C^{12}H^{12}O^{12}.$$

Tannic acid. Gallic acid. Sugar.

As the number of the assimilated atoms of water is in the present instance unusually high, the question arises, whether tannic acid can be arranged with the other conjugate sugar compounds. According to recent discoveries, these compounds appear to be of far more frequent occurrence in nature than was formerly supposed. They constitute indeed the most common compounds.—Liebig's *Annalen*, Feb. 1852.

ANALYTICAL CHEMISTRY.

On a Method of separating the Alkaline Sulphurets from Alkaline Carbonates, Sulphates and Hyposulphites. By G. Werther.

When the salts mentioned above have to be separated, as for instance in examining the residues from gunpowder, the mass is mixed

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with water in which carbonate of cadmium is suspended, and the mixture well agitated in a closed flask. There is formed alkaline carbonate and a yellow precipitate of sulphuret of cadmium, which is collected on a filter. No alkaline hyposulphite or sulphate is formed when the substances are not left too long together. The excess of carbonate of cadmium is extracted from the sulphuret of cadmium by acetic acid, or the whole precipitate, together with the filter, immediately oxidized by nitric acid and chlorate of potash. The solution filtered from the sulphuret of cadmium is heated, and mixed with nitrate of silver; the precipitate of carbonate and sulphuret of silver is digested with ammonia, which removes the carbonate and leaves the sulphuret untouched. The silver is precipitated from the ammoniacal solution by chloride of sodium, and the equivalent of alkaline carbonate calculated from the precipitated chloride of silver. The sulphuret of silver is dissolved in nitric acid, and the silver precipitated by hydrochloric acid; the chloride of silver corresponds to half of the sulphur contained in the hyposulphurous acid; we have therefore 1 equiv. AgCl for 1 equiv. KO, 2SO.

From the liquid filtered from the sulphuret and carbonate of silver the excess of silver is first removed, and then the sulphuric acid precipitated by a salt of baryta. We now deduct from the quantity of sulphuric acid obtained so much as corresponds to the amount produced by the decomposition of the hyposulphurous acid, *i. e.* 0·28 part by weight from every 1 part by weight of the chloride of silver obtained from the sulphuret of silver; the remainder then consists of the sulphuric acid which was contained in the substance examined.

The correctness of the determination of the alkali can be checked in the following manner:—The baryta is removed from the preceding solutions by sulphuric acid, and the alkaline carbonate calculated from the dry alkaline sulphate, after deducting the amounts of alkaline sulphuret, sulphate and hyposulphite, ascertained by the previous determinations.

This method can no longer be applied when trithionic, tetrathionic, and sulphurous acid occur along with the preceding. Hyposulphuric acid, on the other hand, does not interfere, owing to the ready solubility of its baryta salt; but this acid is more difficult to oxidize in this salt.—*Journ. für Prakt. Chem.*, vol. lv. p. 22.

New Test for Mercury. By Arthur Morgan.

The following seems to be a novel and hitherto undescribed method of detecting the salts of mercury, either in substance or solution:—

If a strong solution of iodide of potassium be added to a minute portion of any of the salts of mercury placed on a clean bright plate of copper, the mercury is immediately deposited in the metallic state, appearing as a silvery stain on the copper, which cannot be mistaken, as no other metal is deposited by the same means.

By this method, corrosive sublimate may be detected in a drop

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of solution, unaffected either by caustic potash or iodide of potassium. In a mixture of calomel and sugar, in the proportion of 1 gr. to 200, a distinct metallic stain will be obtained with 1 gr., which of course contains $\frac{1}{200}$dth of a grain of calomel; in like manner $\frac{1}{400}$dth of a grain of peroxide of mercury may be detected, although the mixture with sugar is not in the least coloured by it.

With the preparations of mercury in the undiluted state, this process acts with remarkable accuracy: the smallest possible quantity of calomel or peroxide of mercury, such as would almost require a magnifying lens to perceive, placed on copper, and treated with iodide of potassium, will give a distinct metallic stain.

The advantages of this test may be briefly stated as follows:—1st, it is a delicate test, inferior only to chloride of zinc and the galvanic test of zinc and gold; 2nd, it is easy of application; 3rd, it requires a very small portion of the substance to be examined—a matter of no small import; 4th, acting on the insoluble as well as the soluble salts, it obviates the intermediate process of solution; 5th, when it acts, its indications are decisive.

As to the disadvantages, the only one which seems tenable is, that although it acts on minute portions, still that must be in a concentrated condition. For instance, though we may detect the $\frac{1}{1000}$dth of a grain of corrosive sublimate in a drop of water, we cannot detect it in a drachm; but this may, of course, be remedied by evaporation.

Now with regard to the theory of this process, the following seems most satisfactory,—that the iodide of potassium forms a soluble and easily decomposed salt with the various salts of mercury, that is, an iodide soluble in excess of the iodide of potassium.—*Dublin Medical Press*, Dec. 24, 1851; and *Monthly Journal of Medical Science*, March 1852.

New Process for testing Indigo. By R. Lindenlaub.

The author has contrived the following method for testing indigo. According to Bolley*, chlorate of potash is employed for the decomposition of the indigo. For the decomposition of the chlorate, the author proposes sulphite of soda. The process requires—

1. *A Solution of Sulphite of Soda.*—100 grms. of crystallized carbonate of soda are dissolved in 500 grms. of water, and saturated with sulphurous acid prepared from 100 grms. of copper and 400 grms of sulphuric acid.

2. *A Solution of Chlorate of Potash.*—4 grms. of dry chlorate of potash are dissolved in as much water as is necessary to make up 400 cub. centims.

3. *The Solution of Indigo.*—1 grm. of finely-powdered indigo is dissolved in 10 grms. of fuming sulphuric acid, and diluted to 200 cub. centims.

In applying the test, 50 cub. centims. of the indigo solution are measured off by a pipette, poured into a porcelain dish, diluted with 200 cub. centims. of water, and heated to about 122° F., then mixed

* Chem. Gaz., vol. viii. p. 443.

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with 50 cub. centims. of the solution of sulphite, and finally the solution of chlorate of potash dropped in by means of a burette until complete decoloration is effected. In order to judge how the process is going on, the mixture is tested from time to time by a strip of paper, whose colour is best observed by holding it towards the light. The last drops must be added very cautiously; their action may be best detected by allowing them to run down the side of the dish.

When the first experiment is completed, a second is made, with another 50 cub. centims. of indigo solution, to control the result.—*Journ. für Prakt. Chem.*, vol. liv. pp. 113, 114.

PATENT.

Patent granted to D. Julian *for Improvements in extracting the Colouring Properties of Madder.*

This invention consists in certain processes for extracting the colouring properties of madder, and for obtaining a spirit from the water that has been used in the extracting operation.

Madders of all qualities may be treated according to this invention, which is carried into effect as follows:—2 cwt. of madder, reduced to powder, are thoroughly mixed or diluted with from 113 to 118 gallons of water (according to the fineness of the powder); and then the liquid is run through a filter, composed of a woollen cloth fixed upon a frame within a tun or vessel which receives the water, and is furnished with a cock for discharging the same. The filter will contain 6 cwt. of madder, so that when the above operation has been thrice performed, it will be full. The water is then drawn off through the cock into large wooden tuns, and the madder, which is now a wet paste, is put into linen bags or baskets, and subjected to the action of a hydraulic press, in order to extract the remaining water, such water being added to that before drawn off. After the paste has been well pressed, it is placed in sieves heated to from 120° to 160° F.; and when it is perfectly dry, it is reduced to powder, and passed through a sieve. The patentee states, that a given quantity of this product (which he calls flowers of madder), when employed in dyeing, will have a greater effect than a like quantity by weight of the madder from which it has been extracted.

The water collected from the filter and hydraulic press is put into large wooden tuns, placed in a room heated to from 70° to 85° F.; and it is kept in these tuns until alcoholic fermentation takes place, or for the space of five or six days. If by that time the alcoholic fermentation is not produced, the patentee puts into the tun 5 gallons of boiling water, in which 10 or 12 lbs. of barm have been dissolved. On finding that the density of the water, which was from 3° to 8° Baumé when introduced into the tuns, is reduced to from 1° to 2°, he knows that the alcoholic fermentation has been produced; and he then submits the liquid to the process of distillation, in order to obtain a spirit therefrom.—Sealed Sept. 4, 1851.

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THE CHEMICAL GAZETTE.

No. CCXXIX.—May 1, 1852.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the direct Production of the Hydracids by means of porous Bodies. By B. Corenwinder.

When Dœbereiner made known the remarkable property which finely-divided platinum possesses of exciting chemical actions, it was easy to foresee that this curious fact would lead to numerous interesting discoveries, both in a scientific and in an industrial point of view, and in throwing light upon the theory of several natural phænomena.

Thus all chemists are acquainted with the advantage M. Kuhlmann derived from the use of finely-divided or spongy platinum in determining certain curious reactions, which enabled him to explain in a satisfactory manner the phænomenon of nitrification. It will also be remembered, that, among other important reactions, he pointed out the preparation of nitric acid from oxygen and ammonia, and reciprocally that of ammonia from hydrogen and nitrous compounds.

The object of the present communication is to make known the results of some new experiments which I have made with porous substances. I have succeeded with their aid in combining hydrogen with different metalloids, such as iodine, bromine, sulphur and selenium, with which it does not combine by the action of heat alone. I generally made use of spongy platinum, except in those cases where this substance would have been acted upon by the metalloid employed. In such cases I used in its stead fragments of pumice-stone.

I have in this manner been able to produce directly the following mineral hydracids:—With spongy platinum, hydriodic and hydrobromic acids; with pumice-stone, hydrosulphuric and hydroselenic acids.

Phosphorus and hydrogen are without action on each other when passed through a tube containing pumice-stone, and heated gradually to redness.

Hydriodic Acid.—Hitherto it was impossible to combine iodine and hydrogen directly, even by passing simultaneously these two substances through a porcelain tube heated to redness; but if spongy platinum which has absorbed iodine vapour is submitted to the action of a current of dry hydrogen in a glass tube at a moderate heat, there is immediate production of dense vapours of hydriodic acid

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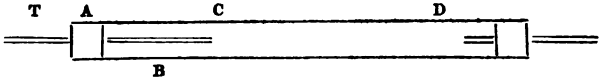
mixed with the excess of hydrogen; however, in operating in this manner, a large amount of unaltered iodine is carried away with the hydrogen, and it is preferable that the vapour of iodine should come successively into contact with the platinum sponge, which I effect by the following arrangement:—I pass a slow current of washed



and dried hydrogen through the tube T, which penetrates about 1 decimetre into the principal tube. Between A and B the space is filled loosely with asbestos, between B and C with iodine, and from C to D with recently-calcined platinum sponge. As soon as the apparatus is filled with hydrogen, I heat the platinum to between 600° and 700°, and then cause a very gentle disengagement of vapour of iodine, in order that none may escape combination. A tube containing a little sulphuret of carbon may be adapted to the apparatus to retain the iodine, and then one or two flasks containing distilled water to absorb the hydriodic acid formed. In a short time a solution is obtained, which has only to be heated to ebullition to expel the little sulphuret of carbon carried over by the current of hydrogen, and the acid is then perfectly pure.

Hydrobromic Acid.—It is well known that M. Balard succeeded in combining bromine and hydrogen directly by passing the two simultaneously through a red-hot porcelain tube. Under these circumstances the action is necessarily restricted. I have succeeded in rendering it more complete by means of platinum sponge, and in producing very pure hydrobromic acid in a short time.

My apparatus consists of a glass tube filled with platinum sponge, to which is adapted a small retort containing bromine, and a flask with its accessory tubes for the disengagement of pure dry hydrogen. The retort is placed in a water-bath, which is kept at a moderate temperature, and the tube is gently heated. By operating carefully, the whole of the bromine is converted into hydrobromic acid, which is collected in water.

Hydrosulphuric Acid.—By passing vapour of sulphur and hydrogen through a glass tube containing fragments of pumice-stone heated to about 700°, hydrosulphuric acid is produced in large quantity. The arrangement of the apparatus is the same as for the hydriodic acid. The sulphuretted hydrogen can be collected in an alkaline solution or in distilled water.

Hydroselenic Acid is readily obtained by operating under the same conditions.

These experiments demonstrate synthetically the composition of hydriodic, hydrobromic, hydrosulphuric and hydroselenic acids; not that there was any doubt on the subject, but it is evident that the interest of science is increased when the proofs are multiplied, and when the two methods of investigation, analysis and synthesis, lead to the same results.

The employment of porous bodies in chemical reactions is de-

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serving of serious attention; there exists in these bodies a powerful and cheap force, which enables us to moderate the action of heat, and which is perhaps destined to find its way some day into some manufacturing processes.—*Ann. de Chim. et de Phys.*, Jan. 1852.

On Lactic Æther. *By* Dr. A. Strecker.

Several fruitless attempts have been made to prepare the æther of lactic acid; this is now readily explainable from the fact, that this compound, which I have obtained by the distillation of dry lactate of lime with sulphovinate of potash, is most readily resolved in the presence of water into lactic acid and alcohol. It is a very mobile colourless liquid, of a faint odour, which dissolves a large amount of chloride of calcium, forming a syrupy liquid, from which a compound of lactic æther with chloride of calcium separates in the cold in colourless acicular crystals. It furnishes at a gentle heat pure lactic æther, which has a neutral reaction, mixes with water (or solution of chloride of calcium) in every proportion, but *immediately* acquires an acid reaction. I have combined the acid liberated from the æther with lime, and found the composition of the lime salt to be $CaO, C^6 H^5 O^5 + 5HO$; it was therefore the ordinary lactic acid. According to my determinations of the chlorine and calcium and combustions, the formula of the chloride of calcium compound is—

$$C^{20} H^{20} O^{12} + CaCl = 2(C^4 H^5 O, C^6 H^5 O^5) + CaCl.$$

It has long been known that several kinds of æther dissolve a considerable amount of chloride of calcium, but only rarely has a crystalline compound of chloride of calcium with a compound æther been prepared.

The composition of this compound favours the view that lactic acid is bibasic, as long considered by Gerhardt, but first clearly proved by Engelhardt and Maddrell by the preparation of acid lactates. I have prepared a double salt of lactic acid, which contains potash and lime, clearly showing the bibasic nature of this acid. If, for instance, a solution of lactate of lime be half precipitated with carbonate of potash and evaporated, hard colourless crystals separate from the hot concentrated solution, which according to my analysis have the composition $KO, CaO, C^{12} H^{10} O^{10}$. They dissolve easily in water, and lactate of lime crystallizes from the *dilute* solution; but on concentration the double salt is again obtained.—Liebig's *Annalen*, Feb. 1852.

On the Resin of the Pitch-Tree and Elemi Resin. *By* S. Baupp.

The resin of the pitch-tree, *Arbol-a-brea* (the tree, according to the author, appears to be the *Canarium album*, Roeush, Decan. Prodr., ii. p. 80, one of the Terebinthaceæ), which was first brought to Paris in 1820 from the Philippines by Perrottet, is so common in

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Manilla that it is used for caulking ships, and has already been examined by Maujean and Bonastre. Maujean found it to consist of 2 parts, one soluble in cold, the other only in hot alcohol. Bonastre found in it—

Soluble resin	61·3
Crystalline sub-resin	25·0
Acid	0·5
Volatile oil with the odour of lemons	6·3
Bitter extract	0·5
Wood and earthy impurities	6·4

The resin with which the author made his experiments possessed some resemblance to elemi-resin; its odour resembled that of fennel, lemons and turpentine. The resin is not homogeneous, but consists of translucent gray or yellowish masses, which in appearance and fracture resemble flint; it becomes somewhat soft in the fingers and adhesive. Other parts have a smoky-gray or blackish colour, which arises from the circumstance that in Manilla the tree is surrounded by fire in order to hasten the efflux of the resin from the wounds. The author has found in this resin,—1st, volatile oil; 2nd, amyrine; 3rd, amorphous resin; 4th, breine; 5th, bryodine; 6th, breidine; 7th, various saline extractives with earthy or saline impurities.

1. *The Volatile Oil* is obtained by distilling the resin; it is lighter than water, and of an agreeable odour; from 7 to 8 per cent. is obtained from the resin.

2. *Amyrine.*—On treating the resin with cold alcohol of 0·848, an insoluble residue is left; this dissolves almost entirely on being boiled with alcohol of 0·833–0·815. On cooling, a sub-resin crystallizes in fine needles, so that the liquid forms a magma; the solid mass is repeatedly exhausted with alcohol of 0·848, and purified in the usual manner. As this substance, according to the author, is identical with the semi-resin of elemi, he retains for it the name amyrine. Amyrine, the sub-resin of the Arbol-a-brea, has already been described by Maujean and Bonastre. The resin furnished about one-fourth of its weight of amyrine.

According to Dumas' analysis, it has the composition $C^{40}H^{33}O$, *i. e.* the same proportions as Hesse found in the analysis of the sub-resin of elemi. The following is the per-centage composition:—85·41 carbon, 11·74 hydrogen, 2·85 oxygen.

Amyrine is readily soluble in æther, from which it crystallizes in very fine slender needles of a silky lustre. It dissolves abundantly in hot absolute alcohol, the greater portion again separating on cooling; water causes the solution to congeal. Water has no action on it. Oil of turpentine and oil of bitter almonds dissolve it more when heated than in the cold. It melts at 345° F. to a colourless liquid, which solidifies into a transparent mass. Nitric acid does not act upon it in the cold; on the application of heat, it deposits a yellow resinous acid substance.

3. *Amorphous Resin* is contained, along with the volatile oil,

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breine and amyrine, in the cold extract obtained with alcohol of 0·848. This extract is distilled with water, when the oil passes over; the residue in the retort is heated to expel the alcohol, when a semi-fluid resin, consisting of a mixture of amorphous resin and breine, floats upon the aqueous liquid. When treated for some time with alcohol of 0·933, it constitutes when dry the soluble resin of Maujean and Bonastre. To obtain the amorphous resin of the author, the breine is separated with the amyrine, for which purpose the semi-fluid soft resin is dissolved in alcohol of 0·848, and allowed slowly to evaporate spontaneously. A crystalline mass separates, which consists of breine mixed with some amyrine; the supernatant alcoholic liquid contains the amorphous resin, which is separated by an addition of water. It is collected and dried, when it forms an inodorous, amber-coloured, fragile mass, which exhibits not the least trace of a tendency to crystallize, and certainly still contains breine.

4. *Breine.*—Its preparation has been described in the preceding paragraph. The author obtained about 1 per cent. from the resin. It crystallizes in transparent rhombic prisms of 70° and 110°, which are insoluble in water, soluble in 70 parts alcohol of 0·848 at 68° F., more readily soluble in absolute alcohol, very soluble in æther; and it melts at 369° F. into a colourless transparent liquid: it is an indifferent resin.

5. *Bryodine.*—The aqueous liquids, containing a little alcohol, which were obtained in the preparation of the amorphous resin 3, and the breine, were further evaporated. As soon as the alcohol is removed, an organic substance begins to separate in oily drops, which subsequently loses its fluidity and becomes more resinous. It is boiled long and repeatedly with water, when it diffuses an odour of peppermint or cardamoms, which subsequently turns terebinthaceous. From the water with which the resinous mass is boiled, a white fibrous substance, bryodine, separates. By repeated ebullition in boiling water and allowing it to cool, it is obtained crystallized and perfectly white. Bryodine separates from an aqueous solution in fine filamentary crystals; the taste is slightly bitter, acrid, or a little pungent. The vapour excites coughing; it melts at 275° to a colourless liquid, which by cooling suddenly solidifies into a warty fibrous mass. It sublimes previous to fusing, and no residue is left in the volatilization; the sublimate has a moss-like appearance, and separates most readily in this form; it may be produced in a couple of seconds between two watch-glasses. It is sparingly soluble in cold water, soluble in 350 parts of water at 50°, more soluble in hot water. The fused mass must be previously reduced to powder when it is wished to dissolve it in water. It is readily soluble in alcohol, æther, oil of turpentine and fatty oils. Acetate of lead and the basic acetate precipitate the aqueous solution; but not so the salts of copper, silver, mercury and iron, or tincture of galls. In alkaliferous water it dissolves unaltered; it likewise dissolves in concentrated acetic acid, but water partially precipitates it from this solution. Strong sulphuric acid dissolves it

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immediately, and is coloured red, and on heating brown. A little nitric acid added to the aqueous solution of bryodine produces a turbidness, but it soon becomes transparent again, and deposits little drops. Nitric acid poured upon bryodine dissolves it; a yellowish oily liquid forms, which floats on the surface of the liquid, and dissolves on the application of heat.

6. *Breidine.*—All the aqueous mother-liquors which are left in the preparation of the two preceding substances, are further evaporated; when highly concentrated, two layers form; the lower one contains some salts, among which chloride of potassium is predominant; the upper, coloured, oily, or bituminous layer was diffused in boiling water, the liquid filtered and evaporated to a syrup, in which, after a time, crystalline crusts of breidine formed.

Breidine crystallizes in rhombic prisms, which terminate in a four-sided pyramid; the surfaces of the prism have an inclination of 102° and 78°. It dissolves in 260 parts of water at 50°, is far more soluble on the application of heat, dissolves sparingly in æther, and readily in alcohol. When heated, the transparent crystals become opake, melt somewhat above the boiling-point of water, and volatilize completely without decomposition. The vapour excites coughing; the aqueous solution gives a white precipitate with basic acetate of lead, but no precipitate with any of the other reagents above mentioned.

7. The residual mother-liquor still contains some inorganic salts and an acid in very small quantity, which was not further examined.

Elemi Resin.—On account of the great similarity of the two resins, the author was induced to make some comparative experiments with elemi resin; he found it to contain a crystalline substance, elemine, which separates in small, transparent, colourless, six-sided prisms, sometimes also in acute rhombohedrons, melts at 392°, dissolves in 20 parts of alcohol of 0·839, is moreover soluble in absolute alcohol and in æther, but insoluble in water.—*Journ. de Pharm. et de Chim.*, xx. p. 321.

On Inosite. *By* Dr. J. Scherer.

The author applied the name of inosite to a kind of sugar which he discovered in 1850 in the fluids of the flesh. As it appeared not improbable that the inosite was a product of decomposition, resulting from the action of sulphuric acid upon some other substance, he has varied the mode of preparation. Formerly the author evaporated the liquid, which had been heated in order to coagulate the albumen; and after the kreatine had crystallized out, removed the baryta from the mother-liquor by sulphuric acid, distilled the filtered liquid, and mixed the residue in the retort with alcohol. In order to avoid the influence of the sulphuric acid, the baryta was not wholly removed. The volatile acids, rendered free, were now taken up by agitating with æther, after which alcohol was added. The inosite separates in a pure state, and in large crystals, and is therefore evidently no product of decomposition by sulphuric acid.

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Inosite has a peculiar reaction. When evaporated with nitric acid upon platinum foil nearly to dryness, and then ammonia and chloride of calcium added, and again evaporated to dryness, the platinum foil exhibits a rose-red colour. If the solution in nitric acid is slowly evaporated on the water-bath, the residue dissolved in water, and set aside in a closed vessel, it becomes mouldy, and then, instead of the above reaction, exhibits a violet-brown colour. —*Journ. für Prakt. Chem.*, liv. p. 705.

On a new Alkali derived from Piperine. *By* A. CAHOURS.

In an investigation published in the 70th volume of the Annalen der Chemie und Pharmacie, MM. Rochleder and Wertheim announce, that by submitting a mixture of soda-lime and piperine to distillation, a volatile oily base is obtained, which possesses all the properties of *picoline*. Wishing to make a comparative study of this base and its isomer, aniline, I distilled, according to their directions, 1 part of pure piperine with 2½ to 3 parts potash-lime. The product, collected in a cooled receiver, consisted of water, two distinct volatile bases, and a trace of a neutral substance of an agreeable aromatic odour, resembling that of the derivatives of the benzoic series. By treating the crude liquid with pieces of caustic potash, a light oily matter separates, which is soluble in every proportion in water, and which on distillation passes over almost entirely between 221° F. and 226°; towards the end the thermometer ascends rapidly to 410°, and remains nearly stationary. The more volatile product, which forms about nine-tenths of the crude product, on fresh rectification passes over at 212°. It is a colourless liquid, with a strong ammoniacal odour, at the same time resembling that of pepper; turns red litmus-paper strongly blue, has a very caustic taste, and saturates the strongest acids. It dissolves in every proportion in water, to which it communicates very marked alkaline properties. This solution behaves like ammonia with respect to saline solutions, excepting that it does not appear to redissolve the oxides of copper and zinc. This base forms, with hydrochloric, hydrobromic, hydriodic, sulphuric, nitric and oxalic acids, perfectly crystalline compounds. The hydrochlorate gives, with the chloride of gold, a crystalline powder, consisting of little needles of a golden colour; and with the bichloride of platinum, a compound which crystallizes in long orange needles, which may be obtained of considerable size by slow crystallization.

Several concordant analyses of this substance have furnished numbers leading to the formula $C^{10} H^{11} N$, which has been checked both by the analysis of its salts and of some derivatives, and by the density of its vapour, the preceding formula representing 4 vols.*

* This base is evidently identical with that obtained by Dr. Anderson by the action of nitric acid upon piperine, and described by him at the Meeting of the British Association held at Edinburgh in 1850, as will be seen from the following abstract of his paper, which appears in the Report for that year, p. 47:—

"Piperine, when treated with nitric acid, is rapidly acted on, with the evolu-

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If we endeavour to ascertain whence the preceding product is derived, we are led to admit that it might belong to the amylene series, $C^{10} H^{10}$, one of the three molecules of hydrogen of the ammonia being replaced by the residue $C^{10} H^{9}$. I therefore attempted to reproduce the above compounds by causing brominated amylene, $C^{10} H^{10} Br^{2}$, to act upon ammoniacal alcohol in closed tubes, in the hope that this compound would behave in an analogous manner to hydrobromic æther. The two liquids mix readily without any particular result; on keeping the mixture for several days at 212°, a deposit of hydrobromate of ammonia is formed, which gradually increases. After several days, when no more of this salt appeared to be deposited, I broke the tube, and treated the residue with water; a heavy, very mobile, volatile, oily liquid separated, which was the product $C^{10} H^{9} Br$, the compound which is immediately formed when $C^{10} H^{10} Br^{2}$ is acted upon by an alcoholic solution of potash.

The liquid, which was strongly ammoniacal, was evaporated to dryness, and the residue treated with strong alcohol, to which it yielded but a very minute quantity of a crystalline substance, from which potash separated an oily matter of a strong ammoniacal odour; but although I operated upon 75 grms. of brominated amylene, I did not obtain a sufficient quantity of the product for analysis. I was not more successful on substituting the compound $C^{10} H^{9} Br$ for the brominated amylene: this has not the least action upon an alcoholic solution of ammonia even after fifteen days' contact at 212°.

Brominated æthylene, propylene and butylene behave precisely like the brominated amylene towards an alcoholic solution of ammonia; consequently the compounds $C^{4} H^{3} Br$, $C^{6} H^{5} Br$, $C^{8} H^{7} Br$ and $C^{10} H^{9} Br$, in the nascent state, that is to say under the most favourable circumstances, do not behave like hydrobromic æther and its analogues.

The new alkali derived from piperine, which I shall call *piperidine*, on being placed in contact with hydriodic æther, becomes heated to such a degree that a portion of the substance would be projected from the vessel if care were not taken to mix very small quantities at a time and to cool well. The mixture, on being heated in closed tubes in an oil-bath, congeals into a mass of beautiful white crystals, which on being decomposed by potash yield an oil, the odour of which is analogous to that of piperidine, but is less ammoniacal. This product, which boils at 262°, has the composition $C^{11} H^{15} N = C^{10} H^{10} (C^{4} H^{5}) N$, which is confirmed by the analysis of its salts and the density of its vapour. The piperidine has consequently exchanged, in the presence of hydriodic æther, 1 equiv. hydrogen for 1 equiv. $C^{4} H^{5}$; it is æthylopiperidine.

tion of nitrous fumes, accompanied by an odour resembling that of oil of bitter almonds. A brown resin is obtained as the result of the action, which dissolves in potash with a magnificent blood-red colour, and on ebullition evolves a volatile base with a peculiar and somewhat aromatic odour. This base gives with hydrochloric acid a beautiful salt, crystallizing readily from alcohol in needles nearly an inch long; and with bichloride of platinum, a salt in beautiful orange prisms, which on analysis yielded results corresponding to the formula $C^{10} H^{11} N HCl, PtCl^{2}$, that is, to a base differing from valeramine by H^{2}."—W.

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The iodides of æthyle and amyle behave in the same manner, and yield—

Méthylopiperidine.. $C^{12}H^{13}N = C^{10}H^{10}(C^2H^3)N$, boiling at 243°.
Amylopiperidine .. $C^{20}H^{21}N = C^{10}H^{10}(C^{10}H^{11})N$, boiling at 367°.

On mixing æthylopiperidine with a fresh quantity of hydriodic æther, it scarcely becomes heated; but on keeping the mixture for some days at 212°, it furnishes a hard crystallizable substance, which dissolves in alcohol, and separates in beautiful crystals on evaporation. This compound, on being heated with caustic potash or submitted to distillation, is resolved into hydriodic æther and æthylopiperidine. It corresponds therefore to the iodide of tetramethyle ammonium and tetræthylammonium. The iodide of amyle gives similar results.

It results from the preceding facts, that piperine is an imidogen base, *i. e.* results from the substitution of two different groups for 2 equivs. of hydrogen. We may therefore write the formula of piperidine in the following manner:—

$$N\left\{\begin{matrix} H \\ C^x H^y \\ C^{10-x} H^{10-y}. \end{matrix}\right.$$

I have not hitherto been able to determine the values of x and y, but I am inclined to believe that the constitution of this base is expressed by the formula—

$$N\left\{\begin{matrix} H \\ C^4 H^3 \\ C^6 H^5, \end{matrix}\right.$$

the hydrogen being replaced in part by æthyle and in part by allyle.

Piperidine, when placed in contact with sulphuret of carbon, becomes much heated, but no gas is disengaged; the product which crystallizes from an alcoholic solution in symmetrical oblique prisms, sometimes of considerable size, results from the simple union of piperidine and sulphuret of carbon.

With the chlorides of benzoyle and cumyle piperidine gives beautiful crystalline compounds, analogous to benzamide and cuminamide. The sulphate, boiled with cyanate of potash, gives piperidic urea; the same compound is obtained by passing moist chloride of cyanogen into piperidine, when there is simultaneously formed some hydrochlorate of piperidine. Dry chloride of cyanogen furnishes hydrochlorate of piperidine and a liquid product, which is analogous to cyanamide, and which is converted in the presence of water into piperidic urea. Lastly, piperidine furnishes, when treated with chlorine and bromine, oily products, which no longer possess basic properties.—*Comptes Rendus*, March 29, 1852.

On the Hydrated Peroxide of Iron and Magnesia as Antidotes in poisoning with Arsenic. *By* J. Haidlen.

The author has satisfied himself by experiments, that to completely precipitate 1 part of arsenious acid within five minutes by

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hydrated oxide of iron, 22 parts of the latter are required. Some which had been kept for a year had lost more than two-thirds of its power; in another case it had lost one-third of it. As is well known, on account of this property of the hydrated oxide of iron, Fuchs has recommended the mixture of hydrated peroxide of iron and magnesia, *i. e.* the mixture of a solution of persulphate of iron, which yields from 17 to 18 per cent. of the hydrated peroxide dried at 212° F., with excess of caustic magnesia. In the Wurtemberg Pharmacopœia the mixture of perchloride of iron with excess of magnesia is prescribed. The author finds that both mixtures precipitate the arsenious acid equally as well as the pure hydrated peroxide of iron, so that there is no chemical objection to their use.—*Jahrb. für Prakt. Pharm.*, vol. xxiii. pp. 196–202.

ANALYTICAL CHEMISTRY.

Application of Metallic Reduction by the Wet Method to Qualitative Analysis. *By* Prof. FISCHER.

THE following notes upon the application of reductions by the moist method were found among the writings of the late Prof. Fischer. The process of using these reductions in qualitative analysis is based upon the circumstance, that many metals are reduced from their solutions by others, whilst others effect these reductions. In these reductions other phænomena occur, as is well known, besides those occasioned by the mere tendency to combine with oxygen; and, as the author showed in 1830, the metals in regard to this property may be divided into the *reducible*,—gold, platinum, silver, mercury, palladium, antimony, copper, bismuth, tin, lead and cadmium; and the *reducing metals*,—zinc, cadmium, iron, tin, lead, cobalt, bismuth, nickel, antimony, mercury, silver and palladium.

The process consists in immersing in the liquid to be examined, (in most cases a few drops are sufficient) first zinc, and when this no longer causes precipitation, cadmium, then iron, &c. To detect the individual metals specially, a number of plates of the reducible metals and rods of the reducing metals must be kept. Both the plates and the rods must be connected with each other by a hinge.

The object of this apparatus is, on the one hand, to allow of any of the metals composing it to be used as a reducer, and, on the other hand, to be enabled to obtain a galvanic circuit by the two combined. A drop of the liquid to be tested is placed upon the rod of the non-reducing metal, the electro-negative component of the circuit, and this is brought into contact with the other reducing metal, the electro-positive metal of the circuit. If now a single reducing metal only be used, the reducible metal separates upon this. If the galvanic circuit be now used, the reducible metal separates upon the negative, not the positive element, and is thus detected with certainty, especially when attention is paid to the colour

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of the metal in the selection of the negative element. If that circuit be taken in which gold or copper exist as negative metals, a white or gray metal is then easily detected, and *vice versâ* when coloured metals are sought for; these are best recognised in the circuit with silver or platinum as the negative metal.

In the further description of the method, let it be supposed that a muriatic solution contains all the reducible metals. In this case a considerable separation will be produced by a zinc rod.

1. A little of the solution is now placed upon the silver plate (of the zinc-silver circuit?). Gold, platinum, and palladium separate upon it with the chloride of silver formed.

2. When the silver ceases to act, the solution is removed, and placed upon the gold plate of the bismuth-gold circuit. The following metals are separated,—antimony as a crystalline easily washed-off powder, and mercury, which adheres firmly to the gold as an amalgam.

3. The solution is removed from the gold plate, by means of a pipette, to a plate of silver or platinum, and a rod of iron introduced into it. Copper is separated upon the plate as a red firmly-adherent precipitate.

4. The solution freed from the copper is divided into two parts; one of these is boiled, to separate the tin, in a test-tube with a plate of lead; the other with a plate of tin, to separate the lead. In this case the application of a circuit, instead of the simple metal, is of no use.

5. Cadmium is detected in the solution 3 after it has been freed from the copper, and any lead present precipitated by sulphuric acid, by immersing a rod of zinc in it.

If the liquid is a nitric and not a muriatic solution, the method remains the same, except that silver may then be present, which is detected in a special manner. All those metals precipitable by iron are then thrown down, to which the silver as nitrate does not belong, and the solution, after this treatment, is placed upon a superficially-amalgamated plate of gold; the liquid, however, must not contain any free acid. If silver be present, the gold is deprived of the mercury at the spot where the solution lies upon the amalgam, and becomes yellow; beyond this the silver separates in a dendritic form.

The above precipitate 1, which is formed upon the silver plate, may contain gold, platinum and palladium. To detect these, the solution is placed upon a plate of palladium. If gold alone be present, the plate becomes yellow. If platinum only be present, the palladium has no action upon it at ordinary temperatures; and on applying heat, the protochloride of platinum separates, which is easily washed off. If no separation is produced by palladium, the precipitate upon the silver itself consists of palladium. From the above description, the methods of quickly detecting small admixtures of metallic salts are evident. Thus by the platinum-iron circuit, copper is readily detected in nitrate of silver, in salts of lead,

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and salts of iron; and mercury in salts of silver by the iron-gold element, &c.

In particular instances, a small pile of from 8 to 10 single-inch copper and zinc plates, with interposed pieces of paper soaked in solution of common salt, is more useful than a simple circuit. By this, iron, zinc, cobalt, nickel, and manganese may be reduced. The poles must consist of platinum or gold wire. The metal is deposited upon the negative pole, and is recognised by the colour of its solution when the wire is moistened with a drop of muriatic acid.—*Journ. für Prakt. Chem.*, vol. liv. pp. 347–357.

On a quick Approximative Method of estimating minute Quantities of Iron by means of a Colorimeter. By THORNTON J. HERAPATH.

The author having been much occupied with the analysis of waters containing minute quantities of iron, and finding the ordinary mode of estimation by precipitation and weighing very troublesome and inaccurate, when applied to such quantities, was led to avail himself of the following centigrade method, founded on the reaction of per-salts of iron with sulphocyanide of potassium. A standard solution of perchloride of iron, containing a little less than $\frac{1}{100}$dth of a grain of metallic iron per cent., was prepared by dissolving 1 gr. of iron in hydrochloric acid, with the addition of a little nitric acid, evaporating nearly to dryness, and diluting to 10,000 grain measures with distilled water at 60°; and from this other standard solutions of different strengths were formed. A convenient quantity of the water, generally half a gallon, was evaporated to dryness, and the saline mass so obtained was afterwards dissolved in hydrochloric acid. The iron contained in the solution having been converted into perchloride by boiling with a few drops of nitric acid, the silica and other insoluble substances were separated by filtration, and the peroxide of iron precipitated by ammonia. This latter precipitate was collected on a filter, and well washed with water. It was then redissolved in the smallest possible quantity of hydrochloric acid; and the liquid having been introduced into a phial or tube of known capacity, was diluted with distilled water until it reached a particular mark upon the side, corresponding to 1000 water-grain measures, care being taken of course to add previously a few drops of a solution of sulphocyanide of potassium. The depth of tint was then compared with that of the standard solutions before mentioned, contained in tubes or phials of similar diameter, in which certain known quantities of iron, ranging from the $\frac{1}{1000}$dth to the $\frac{1}{4}$th of a grain, were contained in the same bulk of water. In order to render the comparison of tints more perfect, the tubes were placed against a sheet of white writing-paper, and held between the eye and the diffused light. Operating in this way, the author was enabled to estimate the $\frac{1}{1000}$dth of a grain of iron per gallon with the greatest readiness. It was sometimes found preferable to employ but one standard solution. The proportion of iron in the liquid

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tested was then determined by measuring the volume of water that was required to lighten the tint so as to render it identical with that of the normal solution, or *vice versâ*.—*Quart. Journ. of Chem. Soc.*, April 1852.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Preparation of the Oxide of Uranium for Technical Purposes. By C. Gieseke.

In the preparation of small quantities of the oxide of uranium, its solubility in carbonate of ammonia is turned to account; for procuring it on a large scale, it is better to use carbonate of soda. 100 lbs. of pulverized pitch-blende are stirred into a thin paste in a leaden vessel with 50 lbs. of sulphuric acid and some water. Nitric acid is added to this mixture sufficient to oxidize it; from 12 to 14 lbs. of nitric acid of 1·4 spec. grav. are required for the purpose. The mass becomes very strongly heated, and solidifies on cooling. It is removed from the leaden vessel, and heated in an iron dish, constantly stirring it, until copious fumes of sulphuric acid are disengaged. The still hot perfectly dry mass is thrown into a sufficient quantity of water, in which it dissolves with the exception of silica, basic persulphate of iron, and other insoluble sulphates. The clear decanted liquid is poured into a solution of soda in 10 parts of water heated to 140°, in such a manner that the sulphatic liquid falls in a thin stream into the soda solution, which is constantly agitated, until the latter exhibits a very feeble alkaline reaction. The oxide of uranium dissolves with great ease in the solution of bicarbonate of soda, which is formed. 1 equiv. sulphate of uranium requires 2 equivs. carbonate of soda for complete solution. The alkaline solution of oxide of uranium is filtered, and boiled in a copper or iron vessel, when the oxides soluble in the bicarbonate of soda, as the carbonates of lime, magnesia and copper, separate in the form of a crystalline powder, and are removed by filtration. In case any oxide of uranium should separate at the same time, this is prevented by the addition of a little carbonate of soda. A solution of carbonate of soda and oxide of uranium which contains a little free carbonate of soda can be boiled for hours without any separation of oxide of uranium. The oxide is now obtained by adding dilute sulphuric or muriatic acid to the boiling alkaline solution until it has a faint acid reaction, and the whole of the oxide of uranium has separated as a heavy yellow precipitate. The preparation obtained in this manner is a very pure oxide of uranium and soda; to obtain the potash compound, the above preparation is dissolved in muriatic acid and precipitated with caustic potash; or a solution of potash is employed at the outset instead of soda. The price and richness of the pitch-blende and potash must, in this case, determine which plan is most advantageous.

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The portion of the pitch-blende which is not dissolved by the carbonate of soda consists for the greatest part of peroxide of iron and perarseniate of iron, and contains the vanadic acid present in the pitch-blende. To obtain the vanadic acid, the pressed moist precipitate is mixed with an equal weight of solution of caustic potash of 1·2 spec. grav., and evaporated to dryness in an iron dish; the mass is digested with water, and the filtered alkaline solution saturated with sulphuretted hydrogen. When the solution is gradually mixed with muriatic acid, a brown precipitate of sulphuret of vanadium is first formed, which becomes lighter in proportion as more acid is added, until finally a pale yellow precipitate of sulphuret of arsenic falls, which contains but very little vanadium. The dark precipitate is collected on a filter, and while moist mixed with some concentrated nitric acid, in which it dissolves to a dark green liquid, leaving an insoluble residue of sulphur. The green liquid is evaporated to dryness, heated to expel the nitric acid, and then dissolved in water, when a yellow saturated solution of sulphate of vanadic acid is obtained. This is supersaturated with ammonia, heated to dissolve the whole of the eliminated salt, filtered hot, and set aside to cool. The vanadiate of ammonia separates in the form of a white crystalline powder. The vanadiate of ammonia still held in solution in the mother-liquor is obtained by saturating it with chloride of ammonium.—*Archiv der Pharm.*, lxix. p. 150.

New Method of testing Ultramarine. By Dr. Bernheim.

The author proposes the following practical method for ascertaining the value of commercial ultramarine and its colouring power. 1 oz. of sulphuric acid is diluted with 20 oz. of water. Equal quantities (50–100 grs.) of the series of samples of ultramarine to be compared are weighed off, and each sample placed in a separate glass; so much of the acid is then added that the blue colour is converted into a reddish one, and no blue particles are perceptible. The quantity of sulphuric acid consumed indicates the degree of colouring power. The quantity of acid consumed can be weighed off, but the easiest plan is to use a graduated burette. Should any smalt be mixed with it, it is readily detected, as the sulphuric acid then no longer completely destroys the blue colour of the sample; strong effervescence points to the presence of carbonic acid; the gas disengaged (sulphuretted hydrogen) can also be easily examined for carbonic acid.—*Central Blatt*, March 3, 1852.

Mixtures for Coloured Fires. By Prof. Marchand.

The following recipes for the preparation of mixtures for coloured fires were found among the posthumous papers of the late Prof. Marchand. The materials are rubbed to a fine powder separately, and then mixed with the hand:—

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Red.

61 p. c. chlorate of potash.
16 sulphur.
23 carbonate of strontia.

Purple-red.

61 p. c. chlorate of potash.
16 sulphur.
23 chalk.

Rose-red.

61 p. c. chlorate of potash.
16 sulphur.
23 chloride of calcium.

Orange-red.

52 p. c. chlorate of potash.
14 sulphur.
34 chalk.

Yellow.

61 p. c. chlorate of potash.
16 sulphur.
23 dry soda.

or,

50 p. c. nitre.
16 sulphur.
20 soda.
14 gunpowder.

or,

61 p. c. nitre.
17½ sulphur.
20 soda.
1½ charcoal.

Light Blue.

61 p. c. chlorate of potash.
16 sulphur.
23 strongly-calcined alum.

Dark Blue.

60 p. c. chlorate of potash.
16 sulphur.
12 carbonate of copper.
12 alum.

Dark Violet.

60 p. c. chlorate of potash.
16 sulphur.
12 carbonate of potash.
12 alum.

Pale Violet.

54 p. c. chlorate of potash.
14 sulphur.
16 carbonate of potash.
16 alum.

Green.

73 p. c. chlorate of potash.
17 sulphur.
10 boracic acid.

Light Green.

60 p. c. chlorate of potash.
16 sulphur.
24 carbonate of baryta.

For Theatrical Illumination.

White.

64 p. c. nitre.
21 sulphur.
15 gunpowder.

or,

76 p. c. nitre.
22 sulphur.
2 charcoal.

Red.

56 p. c. nitrate of strontian.
24 sulphur.
20 chlorate of potash.

Green.

60 p. c. nitrate of baryta.
22 sulphur.
18 chlorate of potash.

Pink.

20 p. c. sulphur.
32 nitre.
27 chlorate of potash.
20 chalk.
1 charcoal.

Blue.

27 p. c. nitre.
28 chlorate of potash.
15 sulphur.
15 sulphate of potash.
15 ammonio-sulphate of copper

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The dark blue is rendered still darker by the addition of some sulphate of potash and ammonio-sulphate of copper.—*Journ. für Prakt. Chem.*, lv. p. 250.

On the Prevention of Incrustations in Steam-Boilers. *By* M. Delandre.

The author states, that, after having long experienced great inconveniences in the use of tubular boilers, owing to their incrustation, notwithstanding the employment of various preventives, he has succeeded in perfectly preserving them free from incrustation for the last year, by placing 2 lbs. of protochloride of tin in a boiler which works twelve hours daily with the pressure of three atmospheres, and consumes in this time from 1500 to 1600 quarts of water, and is only emptied and refilled every eight days. For steam-boilers which are emptied every day and are of great power, the consumption of protochloride of tin should be calculated at half a pound for every cubic metre of water evaporated. The protochloride of tin is changed by the water into an insoluble basic and a soluble acid salt, which latter dissolves the earthy and calcareous salts.—*Comptes Rendus*, March 29, 1852.

On Caoutchouc and Gutta-Percha. *By* M. Payen.

M. Payen has engaged in the investigation of the properties of the various kinds of caoutchouc and gutta percha occurring in commerce. The following are his results:

Solid kinds of Caoutchouc.—The kinds distinguished in commerce are:—1. white, opake caoutchouc, in more or less voluminous masses; 2. caoutchouc in leaves or irregular plates, somewhat yellowish and transparent; 3. another kind in thick plates, or spherical, hollow or solid masses of a brownish-gray colour, and opake; 4. brown caoutchouc, of the same form, more or less transparent and yellowish, in thin sections.

Internal structure.—If very thin laminæ of these kinds be examined under the microscope, very numerous pores are observed, which become distended by capillary attraction with those liquids in which they are not soluble.

Action of Water.—The porosity of caoutchouc explains the readiness with which it is permeated by different liquids that exert no chemical action upon it. Water gives interesting evidence of this. Thin sections of dry caoutchouc, of the best kinds, absorbed from 18·7 to 26·4 per cent. of water in a month. The first had expanded to 5, the others to 15·75 per cent. of their volume. In the course of a very long time, thick caoutchouc also absorbs water; it also, on the other hand, dries again very slowly, because the pores of the surface, during their drying, contract, and thus impede the desiccation.

Attention should be paid in commerce to this amount of water present, since the real value of the caoutchouc may thus be dimi-

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nished from 18 to 26 per cent., and the white colour is entirely deceptive as a sign of better quality. Moreover, the inclosed water makes the caoutchouc less tenacious and ductile, and diminishes its extensibility; for it has long been known that its elasticity increases with the temperature, and diminishes as this decreases, and almost ceases at 32° F. Fibres and bands of caoutchouc, when heated from 60° to 77° F. and cooled to 32°, retain their stiffness and extension even at ordinary temperatures, but suddenly contract and recover their elasticity when they are heated to from 95° to 104° F.

The whiteness and opacity of caoutchouc depend almost entirely upon inclosed water, for by complete drying, caoutchouc becomes brown and transparent.

Action of Alcohol.—Anhydrous alcohol, especially when heated to 172° F., permeates caoutchouc. Thin transparent sections, when heated repeatedly with alcohol, in the course of eight days become opake; they increase 46 thousandths in length, and 94 thousandths in volume. They had acquired a considerable adhesiveness even under alcohol. 100 parts had become 118·6, although the alcohol had extracted 21 thousandths of a fatty, fusible, yellowish matter. After the evaporation of the alcohol the sections became more transparent and adhesive than before.

Action of Solvents.—Æther, benzine, oil of turpentine, sulphuret of carbon, and different mixtures of these substances are rapidly imbibed through the pores of the caoutchouc, causing it to puff up, and apparently dissolving it. But what appears here to be solution, is merely the result of the deposition of a solution in the swollen portions, whereby the latter preserves its original form, becomes distended, and is now easily comminuted. By a sufficient quantity of a solvent these two portions may be almost perfectly separated, by renewing the solvent, without comminuting the greatly expanded residue. The easily soluble portion amounted to from 0·3 to 0·7 per cent. of the mass, according to the nature of the latter and that of the solvent. But the properties of the dissolved and undissolved portions after the evaporation of the solvent are different. The residue of the undissolved portion is more tenacious, less adhesive, and contains the greater part of the brown matter. The dissolved portion, especially that first dissolved, is distinctly more adhesive, softer, more elastic, less tenacious, and less coloured.

Anhydrous æther extracts from transparent caoutchouc 66 per cent. of an amber colour, and leaves 34 per cent. of a tawny colour.

Well-rectified oil of turpentine extracts from brown caoutchouc 49 parts of soluble matter of an amber colour, and leaves 51 per cent. of insoluble brown matter. Traces of resin, which the turpentine still contains, make both parts adhesive, and the dissolved portion viscid for a long time. If the vapour of oil of turpentine be urged against caoutchouc, this extracts from it a volatile oil, which may be obtained by distilling off the turpentine in a water-bath from the first distillate. This oil is colourless, and possesses the natural odour of the caoutchouc.

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Increase of Volume.—If a square prism of caoutchouc be placed in the solvent, the manner in which it becomes expanded may be observed. The dimensions of the lateral surfaces become trebled in benzine, anhydrous æther, oil of turpentine, and a mixture of 100 parts of sulphuret of carbon with 4 parts of anhydrous æther. Hence the entire volume had augmented twenty-seven times, although this expansion only extended to the undissolved portion, as the dissolved portion exists in the solvent itself. A mixture of six parts of æther with one volume of anhydrous alcohol swells up the caoutchouc to four times its volume, only dissolving the thinner, less tenacious, but very adhesive part.

In rectified petroleum, in which a portion also dissolves, the undissolved portion swells to thirty times its volume.

That portion of caoutchouc which most resists solution, exhibits a reticulated texture when magnified 300 diameters, the individual fibres of the net-work anastomose, expand and swell in solvents, and contract when dried. Solutions of caoutchouc, when placed under the microscope, acquire the same remarkable structure, which is distinctly observed when the residue upon the object-holder is wetted with water.

The best solvent was a mixture of 100 parts of sulphuret of carbon with from 6 to 8 parts of anhydrous alcohol. This mixture makes the caoutchouc very quickly fluid, and produces a clear solution; the portions first dissolved are however more fluid, those subsequently dissolved becoming more and more like bird-lime.

When twice its volume of anhydrous alcohol is added to the viscid liquid, the caoutchouc is precipitated; the solution contains the fat and the colouring matter with the greater part of the sulphuret of carbon. When the precipitated caoutchouc is now redissolved by the addition of sulphuret of carbon, a perfect solution is obtained, and by repeating this process the solution each time becomes purer.

In Gérard's excellent process for caoutchouc spinning, by which cylindrical fibres are obtained, a dough of caoutchouc is prepared by dissolving the caoutchouc in a mixture of sulphuret of carbon with 5 per cent. of common alcohol, containing 15 per cent. of water. This principally causes the expansion of the caoutchouc without the occurrence of real solution, because the water contained in the alcohol prevents solution from taking place. Gérard has moreover observed, that fibres of caoutchouc, which may be extended to six times their length, might be again extended six times, after exposure to a temperature of 212° F. The original length could thus be extended from 1 to 16625, whilst the diameter is diminished; hence fibres of remarkable fineness are obtained.

From the above facts, it appears that caoutchouc in its different parts exhibits distinct intermediate properties between those of soluble and insoluble substances. It follows moreover that commercial caoutchouc contains in different proportions:—

1, Easily soluble, ductile, adhesive caoutchouc; 2, the but slightly soluble, immediately tenacious, elastic, extensible mixture; 3, fatty

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matter; 4, volatile oil; 5, colouring matter; 6, nitrogenous matters; different amounts of water up to 0·26.

If all the constituents be separated, in no one is the elasticity and the extensibility of the entire mixture to be found.

Gutta percha is still more easily separable by the above-mentioned solvents into two distinct portions, one of which is soluble, the other insoluble, and retains the colouring matters. The other portion is colourless and soluble, even when extracted from the brown products of commerce, and moreover, tenacious, extensible, and altogether possessing the useful properties of the first. Sulphuret of carbon, and still better a mixture of sulphuret of carbon with from 6 to 8 per cent. of anhydrous alcohol, dissolves gutta percha fractionally, but the greater part of it. Naphtha, benzine, alcohol, æther, and oil of turpentine, appear in the cold to take up the immediately soluble portion.—*Comptes Rendus*, vol. xxiv. p. 2–8.

On the Manufacture of Gas from Wood. By Dr. PETTENKOFER.

Two years ago, Dr. Pettenkofer showed by experiment, at a meeting of the Polytechnic Institute of Bavaria, that a very considerable amount of illuminating gas could be disengaged from 2 oz. of wood. Its practicability on a large scale has since been the subject of much doubt. The inventor's process is now in operation at Basle, and it is also about to be introduced at Zurich, Stockholm and Drontheim. The process is said to be far less expensive than the manufacture from fossil-coal, and furnishes a gas which is free from sulphuretted hydrogen, and several useful collateral products, as charcoal, wood-tar and wood-vinegar.—*Central Blatt.*, March 10, 1852.

PATENT.

Patent granted to Gail Borden, Jun., *for Improvements in the Preservation of certain Animal and Vegetable Substances.*

THIS invention consists in combining flour, farina, meal, or pulverized biscuit with a concentrated extract of the nutritive portions of animal flesh, and drying or baking the same, so as to form a portable desiccated meat-bread or biscuit, containing a large quantity of nutriment in a small bulk, and suited for the use of shipping, armies, emigrants, travellers, hospitals, and for family use.

In carrying out this invention, the patentee takes animal flesh, of any kind suitable for eating, that is fat and in good condition; and in order to extract all its nutritive juices, he macerates it by boiling in a quantity of water until all its nutritious or alimentary properties are obtained in the decoction. The extract or decoction is filtered through strainers of wire-cloth, and further defecated by settling; after which it is reduced by evaporation to about the con-

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sistency of thick treacle. The evaporation may be effected in a pan or tub, with a steam-pipe coiled at the bottom, or by the vacuum process employed in sugar-refining; and previous to and during this operation, all the fat or oily matter that rises to the surface is to be skimmed off, or otherwise removed. The animal extract, which has been reduced to the above-mentioned consistency, is mixed with flour, farina, meal or pulverized biscuit, until a dough is formed sufficiently stiff to be rolled into a convenient form, and cut into pieces by a common biscuit machine. By mixing the flour with the extract in a hot state, the dough is rendered stiffer when cold, and more of the extract is combined with a given quantity of flour, which may, if preferred, be kiln-dried. The dough is desiccated in a drying chamber, or baked in a kiln or oven. The heat employed for this purpose may be equal to that of an ordinary oven after a batch of bread has been baked in it. The dough should be baked slowly, and with great care, until it attains the same degree of dryness as the common biscuits or cracknells. The biscuits manufactured in this manner may be ground into meal for greater convenience in cooking, and may be packed, either in the state of meal or unground, in air-tight casks or cases, or in tight bags of gutta-percha, varnished cloth, or other material that will keep out air and moisture.

To make soup, the biscuit is ground or pulverized, and stirred into sufficient cold water to form a thin batter, which is allowed to stand from five to twenty minutes; and then it is added to boiling water, care being taken to stir frequently during the process, especially before it boils. The boiling is continued from ten to thirty minutes, according to the fineness of the biscuit-meal, until it is dissolved in the water; and salt, pepper, and other condiments are added, to suit the taste. 1 oz. of the biscuit will make a pint of soup. Cooked vegetables, of various kinds, may be used in the soup.

It is stated that this biscuit is not liable to the attacks of weevils and other insects, to which ordinary biscuits and most descriptions of food are subject. It is entirely free from oil or grease, and therefore less liable to deterioration. The excellence of the biscuit depends upon the quantity of animal nutritious matter employed in its manufacture. The extract should therefore be reduced, by the process of evaporation, to about one-eleventh of the weight of the flesh, including its proportion of bone and fat: this is the proportion when fat and well-conditioned beef is used. The patentee mixes about 2 parts of the extract with 3 parts of flour, equal to 5 parts; but about 20 per cent. in weight of this is lost in the baking. The biscuit may be prepared for use in a few minutes, even in a chafing-dish, over a few coals or a spirit-lamp. This invention presents another advantage,—the meat-biscuit can be made in the colonies and other countries where meat is abundant and cheap; and, by reason of its concentration and portability, can be exported, at comparatively small cost, to countries where meat is dear and less abundant.—Sealed Sept. 5, 1851.

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THE CHEMICAL GAZETTE.

No. CCXXX.—May 15, 1852.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Combinations of the Oxides of Cadmium and Silver with Carbonic Acid. By Prof. H. Rose.

Oxide of cadmium exhibits a far greater affinity for carbonic acid than for water. The precipitates therefore which are produced in salts of cadmium by a neutral alkaline carbonate contain very little water, and so much carbonic acid that it almost forms a neutral salt with the oxide of cadmium. This is remarkable, since this oxide has but very feeble basic properties, and weak bases generally exhibit no great affinity for carbonic acid.

Neutral carbonate of potash was used for precipitating the carbonate of cadmium, as on the employment of carbonate of soda, the precipitates obtained were exceedingly difficult to wash.

The precipitate which is formed in the cold in concentrated solutions of equivalent quantities of sulphate of cadmium and carbonate of potash, has the composition $10CdOCO^2 + CdOHO + 2HO$; that produced in cold dilute solutions has the same composition, but contains 1 atom more water; that produced in hot concentrated solutions is represented by $50CdOCO^2 + 6CdOHO + 11HO$; and lastly, that formed in hot dilute solutions has the composition $50CdOCO^2 + 9CdOHO + 12HO$.

Owing to the very small quantity of water contained in the precipitates of the carbonate of cadmium, and the great affinity of the oxide of cadmium for carbonic acid, they retain their carbonic acid at a tolerably high temperature. Even when exposed to a temperature of 572° F., their carbonic acid is not expelled, but only some water; and after ignition they still frequently contain traces of carbonic acid if it has not been sufficiently strong and of long duration.

From the greater affinity of oxide of cadmium for carbonic acid than for water, the moist hydrate, when it has been precipitated by hydrate of potash, absorbs carbonic acid from the atmosphere. All the water is expelled at 572°, but it has absorbed carbonic acid and become converted into a basic carbonate of cadmium, $CdOCO^2 + 2CdO$.

It is remarkable that oxide of silver exhibits considerable affinity for carbonic acid, but none whatever for water. When the solution of an equivalent of a neutral salt of silver is decomposed by an equivalent of a neutral alkaline carbonate, neutral carbonate of silver

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without water is obtained whether the solutions used were concentrated or dilute, cold or hot. Only with a large excess of carbonated alkali is a basic carbonate of silver of the composition $3AgO+2CO^2$ produced by boiling.

The carbonate of silver parts with its carbonic acid at 392°, and is converted into pure oxide of silver, which begins to lose oxygen at 482°.

When oxide of silver is precipitated from a neutral solution by lime-water, but so that a portion of the silver salt remains undecomposed, the moist precipitate readily absorbs carbonic acid from the atmosphere. At 212° it has lost every trace of water, and has absorbed a small quantity of carbonic acid. Oxide of silver therefore forms no hydrate, at least none which can exist at 212°.—*Bericht der Berlin Acad.*, 1852, p. 83.

On some new Salts of Mellitic Acid. By Dr. C. KARMRODT.

The acid used for these experiments was obtained pure from the silver salt.

Mellitate of the Protoxide of Palladium is not crystallizable, but is left, on evaporating its solution, as an amorphous brown mass. It is prepared by saturating protoxide of palladium, obtained from a solution of the protochloride by boiling with carbonate of soda.

Mellitate of the Protoxide of Palladium and Ammonia, $PdO, C^4O^3 + 2NH^3, 2HO$, is formed when the preceding salt is dissolved in ammonia. The colourless liquid deposits on evaporation colourless rhombic prisms, which furnished on analysis—

Protoxide of palladium	37·90	37·82	1	37·97
Mellitic acid	29·73	29·65	1	29·79
Ammonia.....	19·65	20·21	2	21·08
Water	12·72	12·32	2	11·16

Mellitate of the Protoxide of Palladium and Soda crystallizes from a strong concentrated solution in triagonal pyramids, each two of which are grown together. It contains 34·0 per cent. of palladium.

Mellitate of the Protoxide of Palladium and Potash is obtained in the same manner as the soda salt. It crystallizes in verrucous groups of indistinct prisms, which deliquesce in the air.

Mellitate of the Protoxide of Mercury, $Hg^2O, C^4O^3 + 2HO$, is precipitated by protonitrate of mercury from a solution of mellitic acid or of an alkaline mellitate as a white, finely granular powder. It is nearly insoluble in water, soluble in nitric acid. The precipitate, dried at 374°, is anhydrous. Dried at 212°, it furnished—

Protoxide of mercury	76·56	1	75·92
Mellitic acid.....	16·85	1	17·52
Water	6·59	2	6·56

Mellitate of the Peroxide of Mercury, $HgO, C^4O^3 + 2HO$.—When peroxide of mercury and mellitic acid are triturated together and

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gently heated, a white granular mass is obtained. Pure mellitic acid, and also the alkaline mellitates, give with a solution of pernitrate of mercury a white bulky precipitate, which dries into heavy hard pieces. This mass dissolves in warm nitric acid; ammonia causes no precipitate in such a solution. The water is expelled at 392°. The salt, dried at 212°, furnished—

Peroxide of mercury	61·50	1	62·08
Mellitic acid.....	28·13	1	27·59
Water	10·37	2	10·33

Mellitate of the Protoxide of Nickel, NiO, $C^4 O^3 + 8HO$.—When a hot solution of mellitic acid is saturated with protocarbonate of nickel, a grass-green semi-fluid mass separates, which on cooling becomes turbid and of firmer consistence, and can be washed by kneading between the fingers. The salt becomes hard and glassy in the air, and resembles chrysoprase. It is sparingly soluble in water, but dissolves readily in dilute hydrochloric and dilute nitric acids. At 212°, this salt loses 1 atom of water; at 356°, 3 more atoms; but the last atom is only expelled at 572°. It gave on analysis—

Protoxide of nickel ..	23·95	23·64	1	23·83
Mellitic acid	30·47	30·20	1	30·49
Water..... 46·24	45·58	46·16	8	45·68

Mellitate of the Protoxide of Nickel, NiO, $C^4 O^3 + 3HO$, was obtained from the concentrated mother-liquor of the preceding salt in delicate rhombic prisms, which are far more soluble in water than the preceding salt. Analysis furnished—

Protoxide of nickel· 32·65	32·27	33·01	1	33·35
Mellitic acid .... 42·92	43·01	42·88	1	42·67
Water..... 24·43	24·69	24·11	3	23·08

Mellitate of the Protoxide of Cobalt, CoO, $C^4 O^3 + 6HO$, separates, on neutralizing a hot solution of mellitic acid with carbonate of cobalt, as a brown smeary mass, which on cooling solidifies to one piece, or as a granular crystalline powder if stirred with a glass rod while cooling. Cold water dissolves $\frac{1}{37,300}$dths, hot water much more. On cooling, the solution deposits a pale reddish powder, which appears under the microscope to consist of short rhombic prisms. Analysis gave—

	Granular.	Pale red powder.			
Protoxide of cobalt	27·00	25·75	26·33	1	26·87
Mellitic acid	34·59	35·03	35·21	1	34·43
Water.....	38·41	39·22	38·46	6	38·70

Mellitate of the Protoxide of Iron, $2FeO, C^4 O^3 + 3HO$.—When mellitate of ammonia is added to protosulphate of iron, a greenish-white precipitate is formed, which again disappears with heat. On ebullition, a lemon-coloured precipitate of basic mellitate of the protoxide of iron falls, which turns light olive-green on desiccation, and consists of microscopic cubic octahedra. The salt is sparingly

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soluble in water, but readily soluble in dilute hydrochloric acid. The whole of the water is expelled at 374°. Analysis gave—

Protoxide of iron	48·80	1	49·00
Mellitic acid	32·51	1	32·65
Water	18·49	3	18·35

Mellitate of the Protoxide of Manganese, MnO, C^4O^3+6HO, is obtained by saturating mellitic acid with protocarbonate of manganese and heating; a white powder falls, which appears under the microscope to consist of fasciculate groups of needles. This salt is more soluble in cold than in hot water, which only takes up $\frac{1}{100}$dth. It furnished on analysis—

Protoxide of manganese	25·75	1	25·85
Mellitic acid	34·24	1	34·91
Water	40·01	6	39·24

Mellitate of Zinc, ZnO, C^4O^3+5HO, prepared from mellitic acid and carbonate of zinc, separates as a crystalline powder, consisting of four-sided rectangular prisms. It dissolves pretty readily in cold water, and the solution deposits a portion of the salt at 120°–140°; it dissolves readily in dilute acids and in mellitic acid; the whole of the water is expelled at 400°. On analysis it furnished—

Oxide of zinc	30·00	29·24	1	30·34
Mellitic acid	36·02	37·55	1	35·97
Water	33·67	33·66	5	33·69

Mellitate of Zinc, ZnO, C^4O^3+3HO.—From the solution of the preceding salt alcohol precipitates another in the form of caseous flakes, which appear under the microscope to consist of a tissue of slender needles. It is more easily soluble than the preceding salt, and contains 2 atoms less water, the whole of which it parts with at 320°. It furnished—

Oxide of zinc	36·12	35·98	1	35·07
Mellitic acid	41·70	42·62	1	41·57
Water	22·35	21·57	3	23·36

Mellitate of Magnesia, MgO, C^4O^3+6HO.—When a warm solution of mellitic acid is saturated with carbonate of magnesia, the salt separates in clear oily drops, which become turbid on cooling, and crystallize on exposure to the air. The salt is very sparingly soluble in water. It parts with 4 atoms of water at 302°, and the whole is expelled at 356°. It gave—

Magnesia	17·53	1	16·83
Mellitic acid	40·17	1	39·16
Water	41·75	6	44·01

Mellitate of Magnesia, MgO, C^4O^3+7HO, is separated by alcohol from the solution of the preceding salt in minute four-sided prisms. The salt gave on analysis—

Magnesia	15·43	1	15·92
Mellitic acid	36·57	1	37·02
Water	48·00	7	47·06

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Mellitate of Strychnine is a crystalline precipitate, which is obtained on mixing an alcoholic solution of mellitic acid with an alcoholic solution of strychnine; it is insoluble in alcohol; cold water dissolves about $\frac{1}{1500}$dth, and boiling water $\frac{1}{650}$th, from which solution it separates on cooling in bundles of silky prisms. The air-dried salt lost at 212°, 1·2 per cent. water; at 248°, 1·7; at 338° it begins to turn yellow and become decomposed. It furnished 20·27 and 20·5 per cent. acid, according to which it appears to contain 2 atoms of mellitic acid to 1 of strychnine.

Mellitate of Quinine is formed when an alcoholic solution of quinine is boiled with mellitic acid as a white bulky precipitate, which becomes crystalline on being washed with weak spirit, and consists of rhombic prisms with a mother-of-pearl lustre; it parts with no water at 212°, but becomes sulphur-coloured at 266°, with loss of some water and ammonia. It appeared to contain 2 atoms of acid to 1 of base; on precipitating with silver, it furnished 37·5 and 38 per cent. of mellitic acid.

Mellitate of Cinchonine is obtained in the same manner as the quinine salt, which it closely resembles. Analysis furnished 37·4 and 36·6 per cent. of acid; it consequently contains 2 atoms of acid.

Mellitate of Morphine.—An aqueous solution of mellitic acid is completely neutralized by morphine; and on evaporating the liquid, a neutral salt is left as a brownish amorphous brittle mass. When morphine is dissolved in a hot concentrated solution of mellitic acid, a white crystalline salt separates, which appears to consist under the microscope of slender needles. It is insoluble in alcohol and æther, rather more soluble in cold than in hot water, and readily soluble in potash and ammonia. At 230° it lost only 2 per cent. in weight. It contained 25·2–24·6 per cent. mellitic acid, according to which it contains 2 atoms of acid to 1 of base.

Mellitate of Solanine is a neutral salt, the solution of which is decomposed on evaporation to dryness. The dry mass contains free mellitic acid and solanine.

Mellitate of Furfurine forms verrucous groups of crystals, which on recrystallization were obtained in monoclinohedral prisms. Between 212° and 257° it loses 5·7 per cent. water. At 266° it begins to turn yellow.

Mellitate of Aniline forms little plates resembling benzoic acid, which are readily soluble in water. The transparent crystalline plates become turbid in alcohol, and are dissolved on the application of heat; the salt cannot again be obtained crystallized from a solution in alcohol. At 212° its weight is not diminished. At 221° it becomes yellowish and loses aniline. It contained 44·9 and 44·4 per cent. of mellitic acid, according to which it appears to contain 2 atoms of acid.

Mellitic Acid and Urea.—No crystals could be obtained from a syrupy solution of equivalents of mellitic acid and urea. Alcohol produced no change in the solution.—Liebig's *Annalen*, lxxxi. p. 164.

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On Dr. Keller's *supposed Formation of Metacetonic Acid from Flour and Leather. By* R. W. Forster.

A mixture of flour with scraps of leather, carbonate of lime and water, having been digested for three weeks at a gentle heat, the liquid was strained off, the dissolved lime salt converted into a soda salt, the solution concentrated by evaporation, and distilled with excess of sulphuric acid. A portion of the acid distillate was then neutralized with carbonate of soda, the remainder added to it, and the whole distilled. According to Keller, butyric æther should distil over, acetate and metacetonate of soda remaining in the retort. The distillate obtained by Mr. Forster, however, had an odour not at all resembling that of butyric æther; and the dry residue, when distilled with sulphuric acid, yielded a distillate which had not the odour of either acetic or metacetonic acid, and gave no odour of acetic æther when heated with alcohol and sulphuric acid. The liquid also yielded a baryta salt containing 65·5 per cent. (mean) of baryta, a quantity differing by 1½ per cent. from 67·4, the amount required by the formiate; the deficiency was probably due to slight impurities. Acetate of baryta contains 60 and metacetonate of baryta 54·06 per cent. of the base. Moreover, the solution of the baryta salt rapidly reduced nitrate of silver. The principal constituent of the distillate appears therefore to be *formic acid.— Quart. Journ. of the Chem. Soc.*, April 1852.

On Paralbumine, a new Albuminous Substance. By Dr. J. Scherer.

The author has examined large quantities of fluids which were obtained in the operative treatment of *hydrops ovarii*, and found that the individual cysts contained, along with ordinary albumen, another albuminous substance, which possesses very distinct characters. The liquid in its original state was slightly alkaline, could be drawn out into threads, and frothed considerably; it mixed pretty readily with water, and deposited after a time a slight sediment. Nitric acid gave a copious precipitate, insoluble in an excess. Hydrochloric acid in small quantity produced no change, in large quantity it caused a slight turbidity. Acetic acid was without any action on it. In the solution acidified by acetic acid, ferrocyanide of potassium gave a copious precipitate. Precipitates were also produced by chromic acid, perchloride of mercury, basic acetate of lead and tincture of galls. On boiling the liquid diluted with water, slight milkiness resulted; on adding acetic acid carefully to the boiling liquid, it became very turbid, and coagulated flakes formed in it; but the liquid did not become clear and capable of filtration, as in the case of albumen, but still remained turbid, and could not be filtered.

When the liquid is mixed with alcohol, a copious precipitate is formed. This, after exhaustion with alcohol, dissolves almost entirely in water at 95° F., and the solution has all the reactions above mentioned. These fluids therefore contain a substance which dif-

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fers from ordinary albumen by the solubility in water of the precipitate produced by alcohol, as also by the imperfect coagulation on boiling with the addition of some acetic acid.

On boiling the substance with a solution of potash, and adding some oxide of lead-potash, the presence of sulphur is readily detected in it. However, except in these differences, it has all the reactions of the albumen from eggs, serum, exudations, &c. It has most resemblance to the albuminous substance observed by Bernard in the pancreas; this however coagulated to a white mass on the application of heat.—*Journ. für Prakt. Chem.*, liv. p. 402.

ANALYTICAL CHEMISTRY.

On Poisoning by Nicotine. By M. Orfila.

The principal object of this paper is to show—

1. That we may characterize pure nicotine as easily as we can a poison derived from the mineral kingdom.

2. That we may detect this alkali in the digestive canal, and demonstrate its existence there, although it is present only to the extent of a few drops.

3. That it is sufficiently easy to prove its presence in the liver and the other organs after it has been absorbed.

1. *Pure Nicotine may be characterized as easily as a Poison derived from the Mineral Kingdom.*—Nicotine, discovered in 1809 by Vauquelin, was studied in 1828 by Messrs. Posselt and Reimann, who found it in different species of *Nicotiana*, in *macrophylla*, *rustica*, and *glutinosa*. Messrs. Boutron, Charlard, and Henry described some of its properties in 1836. Havanna tobacco contains 2 per cent., that of Maryland 2·3, that of Virginia 6·9, that of Alsace 3·2, that of Pas-de-Calais 4·9, that of the Nord 6·6, and that of Lot 8. It is classed among the *natural volatile* vegetable alkalies, which are only three in number, namely *conicine*, *theobromine* and *nicotine*. This last may be represented as a compound of 1 equiv. of ammonia (H^3 N), and of 1 of a hydrocarbon containing 4 equivs. of hydrogen and 10 of carbon (H^4 C^{10}). It is now obtained by a much more simple process than was formerly adopted, which consists in passing the smoke of tobacco into water acidulated with sulphuric acid. Sulphate of nicotine is thus speedily produced, and this has to be decomposed by a strong alkali. It is then only necessary to apply sufficient heat to volatilize the nicotine. This mode of preparation indicates that smokers, in respiring the smoke of tobacco, introduce into their bodies a certain quantity of the vapour of nicotine.

Characters of pure Nicotine.—It forms an oleaginous, transparent, colourless, tolerably fluid, anhydrous liquid, of the density of 1·048, which becomes slightly yellow by keeping, and tends to become brown and thick from contact with the air, from which it absorbs

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oxygen; its acrid odour resembles but slightly that of tobacco; its taste is very burning. It volatilizes at 77° F., and leaves a carbonaceous residue. The vapour which rises presents such a powerful smell of tobacco, and is so irritating, that it is difficult to breathe in a room in which one drop of it has been spilt. If this vapour be approached with a lighted taper, it burns with a white smoky flame, and leaves a carbonaceous residue as an essential oil would do. It *strongly blues* reddened litmus-paper. *It is very soluble in water*, in alcohols and in fat oils, as also in *æther*, which easily separates it from an aqueous solution. The great solubility of nicotine in both water and æther forms an important fact in its chemical history, as the greater number of vegetable alkalies, not to say all, if they dissolve easily in one of these liquids, are not readily soluble in the other.

Nicotine combines directly with acids, disengaging heat. Concentrated pure sulphuric acid, without heat, produces with it a wine-red liquid; on the application of heat, it becomes thick, and acquires the colour of the dregs of wine; if it be boiled, it blackens, and disengages sulphuric acid. With cold hydrochloric acid it disengages white vapours as ammonia does; if the mixture be heated, it acquires a violet colour, the intensity of which increases with prolonged ebullition. Nitric acid, aided with a little heat, imparts to it an orange-yellow colour, and white vapours of nitric acid are first given off, then red vapours of hyponitrous acid. If it be further heated, the liquor becomes yellow, and by ebullition it acquires a red colour resembling that of chloride of platinum. Prolonged ebullition gives a black mass. Heated with stearic acid, it dissolves and forms a soap, which congeals on cooling, and is slightly soluble in water and very soluble in hot æther. The simple salts of nicotine are deliquescent, and difficultly crystallizable. The double salts which it yields with the different metallic oxides crystallize better.

The aqueous solution of nicotine is colourless, transparent, and strongly alkaline. It acts like ammonia towards several reagents; thus it gives white precipitates with bichloride of mercury, acetate of lead, protochloride and bichloride of tin; a canary-yellow precipitate with chloride of platinum, which precipitate is soluble in water; a white precipitate with salts of zinc, which is soluble in excess of nicotine; a blue precipitate with acetate of copper. This precipitate is gelatinous and soluble in excess of nicotine, forming a blue double acetate, similar to that formed by ammonia with the same salt. It gives an ochre-yellow precipitate with salts of the sesquioxide of iron, insoluble in excess of nicotine. With sulphate of protoxide of manganese it gives a white precipitate of protoxide, which speedily becomes brown by contact with the oxygen of the air. It separates the green sesquioxide from the salts of chromium. The red permanganate of potash is instantly decolorized by nicotine, as by ammonia, although this latter alkali acts more slowly, and must be used in larger proportion.

The following reactions may serve to distinguish the aqueous solutions of nicotine from ammonia. Chloride of gold yields a red-

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dish-yellow precipitate, *very soluble in an excess of nicotine.* Chloride of cobalt yields a blue precipitate, which changes to green; the oxide thus formed does not readily dissolve in excess of nicotine, whilst ammonia dissolves the green precipitate and forms a red solution. Aqueous solution of iodine gives a yellow precipitate with solution of nicotine, as chloride of platinum would do; with an excess of nicotine it acquires a straw colour, and it is decolorized by the action of heat. Ammonia, on the contrary, immediately decolorizes the aqueous solution of iodine without rendering it turbid. Pure tannic acid gives with nicotine an abundant white precipitate. Ammonia gives no precipitate, but imparts a red colour*.

If to these chemical characters, which permit one so easily to distinguish nicotine, we add those resulting from the action which it exercises on the animal œconomy, it will no longer be possible to confound it with any other body. The following are the results of the experiments I undertook in 1842 on this alkali, and which I published in 1843. (See the 4th edition of my work on Toxicology.)

First Experiment.—I applied three drops of nicotine to the tongue of a small but tolerably robust dog; immediately afterwards the animal became giddy, and voided urine; at the end of a minute its breathing was quick and panting. This state lasted for forty seconds, and then the animal fell on its right side, and appeared intoxicated. Far from showing any stiffness or convulsions, it was feeble and flabby, although the fore-paws slightly trembled. Five minutes after the administration of the poison, it uttered plaintive cries, and slightly stiffened its neck, carrying the head slightly backwards. The pupils were excessively dilated; the respiration was calm and in no way accelerated. This state lasted ten minutes, during which time the animal was not able to stand. From this time the effects appeared to diminish, and soon after it might have been pre-

* It is interesting to compare the physical and chemical properties of nicotine with those of conicine.

Conicine is yellow; *its smell resembles that of the urine of the mouse*, and differs entirely from that of nicotine; it strongly blues reddened litmus-paper. Added to water and shaken with it, it floats on the surface and is not readily dissolved. Æther dissolves it easily. When heated in a capsule, it forms white vapours, *having a strong smell of celery mixed with that of the urine of the mouse.* Weak tincture of iodine yields a white precipitate, which acquires an olive colour with excess of the tincture. Pure concentrated sulphuric acid *does not alter it*; when the mixture is heated, it acquires a greenish-brown colour; and if the heat be continued, it becomes blood-red and afterwards black. Nitric acid imparts to it a *topaz colour*, which is not changed by the action of heat. Hydrochloric acid yields white vapours as ammonia does, and renders it violet, especially when heated. Tannic acid gives a white precipitate, and bichloride of platinum a yellow precipitate. The red permanganate of potash is immediately decolorized. Corrosive sublimate yields a white precipitate. Acetate of copper gives a gelatinous blue precipitate, less soluble in an excess of conicine than that formed with nicotine. Chloride of cobalt behaves with it as it does with nicotine. Chloride of gold gives a light yellow precipitate. *Neutral acetate of lead does not give any precipitate*, neither does the subacetate. Chloride of zinc gives a white gelatinous precipitate, soluble in excess of the conicine. Sulphate of sesquioxide of iron gives a yellow precipitate. The words in italics indicate the means of distinguishing conicine from nicotine.

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dicted that they would speedily disappear entirely. Next day the animal was quite well. The nicotine I used was evidently not anhydrous.

Second Experiment.—I repeated the experiment with five drops of nicotine on a dog of the same description. The animal showed the same effects, and died at the end of ten minutes; during four minutes he showed slight convulsive movements.

Opening of the Body the day following.—The membranes of the brain were slightly injected, and the superficial vessels were gorged with blood; this injection was especially observed on the left side and in the lower part of the brain. The brain itself, of the ordinary consistence, had the two substances of which it is composed slightly disintegrated, the striated substance was much injected, as well as the *pons varolii.* The membranes which envelope the cerebellum were still more injected than the other parts. Between the first and second cervical vertebræ on the right side, that is on the side on which the animal fell, there was a rather considerable effusion of blood. The lungs appeared to be in their natural state. The heart, the vessels of which were gorged with blood, was greatly distended, especially on the right side, with clots of blood; the auricles and the right ventricle containing much, and the left ventricle none. The superior and inferior *vena cava* and the aorta were equally distended with clots of semi-fluid blood. The tongue was excoriated along the middle line, and towards the posterior part, where the epithelium separated with facility. In the interior of the stomach there were found a black pitchy matter and a bloody liquid, which appeared to have resulted from an exudation of blood. The duodenum was inflamed in patches; the rest of the intestinal canal appeared in a healthy state.

Since the above period I have made the following experiments, which I have frequently repeated with the same results, only that in some cases I have found the blood contained in the cavities of the heart in a fluid state, even when proceeding to dissection immediately after death; nevertheless the blood speedily coagulated.

Third Experiment.—At eleven o'clock I administered to a dog of moderate size, twelve drops of nicotine. A few instants afterwards giddiness came on, and *he fell on the right side*; he soon manifested convulsive movements, slightly at first, then sufficiently strong to constitute a tetanic fit with opisthotonos; he was in a remarkable state of drowsiness, and uttered no cry. His pupils were dilated; there was no action of the bowels nor vomiting. He died at two minutes after eleven. The body was immediately opened. The abdomen and thorax, on being cut open, *occasionally* emitted a very decided smell of tobacco. The heart contained a considerable quantity of *black coagulated* blood. There was more in the right auricle and ventricle than in the left. The lungs appeared in a normal state. The stomach contained about 40 grms. of a thick, yellow, slimy liquid; and here and there parts of the mucous membrane were inflamed. The œsophagus, the intestines, the liver, the spleen, and the kidneys were in a normal state. The epithelium

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was easily detached from the tongue; the base of this organ was red and slightly excoriated. The brain was more injected than its enveloping membranes; the *pons varolii* was the same as in the second experiment.

Fourth Experiment.—I applied, to the eye of a dog of moderate size, one drop of nicotine; the animal instantly became giddy and weak in its limbs; a minute afterwards he fell on his right side and manifested convulsive fits, which became more and more powerful; the head was thrown back. At the end of two minutes the convulsions ceased, and extreme weakness ensued. Five minutes afterwards the animal could stand, but was unable to walk. Ten minutes later he was in the same state without having vomited or had any action of the bowels. Urged to walk, he made a few undecided steps, then vomited about 100 grms. of a grayish alimentary paste. At the end of half an hour he was in the same state. It was evident that he was recovering. The conjunctiva was sensibly inflamed, and the transparent cornea was to a great extent opake.

2. *We may detect nicotine in the digestive canal, and affirm its existence there, although it may be only present to the extent of a few drops.*—I would call the particular attention of the Academy to this paragraph; I have never, in the course of my numerous experiments, seen animals whose death has been almost instantaneous, either vomit or have any action of the bowels*. If it be the same with man, as everything tends to prove it is, the chemist will, under such circumstances, be in the most favourable condition for detecting the poison, as there will most frequently be a sufficient quantity in the canal to determine its presence.

Before describing the two processes to which I had recourse for determining the existence of nicotine in the stomach and intestines, as well as in the œsophagus, it may be observed that I acted separately on the liquid and solid matters contained in these organs, and on the organs themselves.

First Process.—The contents of the stomach and intestines, or the organs themselves, are placed in a considerable proportion of sulphuric æther; after twelve hours of maceration, it is to be filtered; the æther passes through, holding nicotine in solution; most frequently, when the matters on which the æther has acted are fatty, the æther holds in solution a soap composed of nicotine and one or several fatty acids; it may also happen that it contains non-saponified nicotine. The ætherial liquid is evaporated almost to dryness by a very gentle heat. The greasy and soapy product obtained rarely shows any alkaline reaction. It is to be agitated, without heat, with caustic soda dissolved in water, to decompose the soap and set free the nicotine. The whole is then to be put into a retort furnished with a receiver plunged in cold water, and heat applied to the retort until no more liquid remains in it. The liquid condensed in the receiver contains either all, or at least a large proportion of the nicotine. It is well known that,—1st, when heat is applied to the retort, the matter froths, augments in volume, and would cer-

* If life is prolonged, the animals vomit.

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tainly pass into the receiver if the retort was not very large in relation to the quantity of liquid operated upon; 2nd, even at a temperature of 212° F. the vapour of water carries with it a certain quantity of nicotine; therefore the operation should be carried on as much as possible in close vessels. If these precautions be observed, the distilled liquid will be limpid and colourless; it suffices then to concentrate it over a water-bath to about a sixth of its volume, to obtain with it all the reactions of nicotine.

Second Process.—The method of which I am now going to speak is evidently superior to the preceding. The matters contained in the stomach and intestines, or the organs themselves, as well as the œsophagus, are macerated in water acidulated with pure and concentrated sulphuric acid, taking, for instance, four or five drops of acid to 150 or 200 grms. of water. At the end of twelve hours it is to be filtered; the liquid, which is generally of a yellow colour, contains sulphate of nicotine and a certain quantity of organic matter. It is then to be evaporated almost to dryness in a close vessel over a water-bath; then treated with a few grammes of distilled water, which dissolves the sulphate of nicotine, leaving the greater part of the organic matter undissolved; it is now to be filtered; the filtered liquid is to be saturated with a little pure hydrate of soda or potash, in order to combine with the sulphuric acid, and set free the nicotine. The mixture of nicotine and sulphate of soda or potash is to be put into a retort, and heated as described in the first process; the distilled liquid is to be evaporated over a water-bath in order to concentrate the solution of nicotine.

Instead of distilling the liquor by heat, I have often treated it with æther; this latter, decanted and submitted to spontaneous evaporation, leaves the nicotine.

Everything tends to show that nicotine may be detected by other processes. Thus by treating the digestive canal with absolute alcohol, with the addition of a little soda, it would be dissolved, and by the reaction of the soda a soap would be formed with the fatty matter, which would set free the nicotine; it would then only have to be distilled after evaporation to dryness. Perhaps also it might be separated by acting on the tissues with pure soda or potash, then evaporating to dryness, and heating it in closed vessels.

3. *It is sufficiently easy to prove the presence of nicotine in the liver and other organs after it has been absorbed.*—In 1839, when I had shown that poisons, after having been absorbed, might be extracted from the organs where they had been carried with the blood, I insisted so strongly on the necessity of examining these organs with a view to the detection of poisons, that it has now become the custom to proceed in this way. How often does it happen, that, in consequence of repeated vomiting and action of the bowels, and also from complete absorption having taken place, there remains no trace of the poison in the digestive canal! Moreover it is evident that, in getting the poison from the organs to which it has been carried by absorption, we obtain in reality that portion of the poison which has been the cause of death, unless it be shown that it was carried

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to those organs after death by absorption. The livers of those animals which I had poisoned with twelve or fifteen drops of nicotine, when submitted to one or other of the processes I have described, furnished me with appreciable quantities of this alkali. I scarcely obtained any from the blood contained in the heart, but I had only operated upon a few grammes. Moreover, experience teaches that a great number of poisons absorbed rapidly pass from the blood into the organs, and most especially into the liver.

It may be readily conceived that the research for absorbed nicotine might be fruitless in those cases where death was occasioned by only a few drops of this body; but then the presence of the alkali may be detected in the digestive canal.

Gentlemen, after results such as those obtained by M. Stas and myself, society may feel satisfied. Without doubt, intelligent and skilful criminals, intent on puzzling the chemists, will sometimes have recourse to very active poisons, but little known to the community at large, and difficult to detect; but science is on the alert to surmount all difficulties. Penetrating to the recesses of our organs, she extracts evidence of the crime, and furnishes one of the great elements of conviction against the guilty. Do we not know that at the present time poisonings by morphine, brucine, strychnine, nicotine, conicine, hydrocyanic acid, and many other vegetable substances which were formerly believed to be inaccessible to our means of investigation, may be discovered and recognised in a manner to be perfectly characteristic?—*New York Journal of Pharmacy*, Jan. 1852.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Sulphurization of Caoutchouc, and on some Properties of Sulphur. *By* M. PAYEN.

THE discovery in 1843 of the remarkable properties which are communicated to caoutchouc by a peculiar kind of sulphurization, called *vulcanization*, is generally attributed to Mr. Hancock *. It is only from this period that the applications of this elastic substance have become of considerable importance, and have given birth to several new branches of industry. In fact, since then the alterations produced upon the immediate principle, either by an elevation or decrease of the atmospheric temperature, have had no influence upon the vulcanized product. It preserves its suppleness and its elasticity below 32° F., and no longer becomes soft or adhesive above 95° and 104°; its temperature may even be raised beyond 212° without loss of that tenacity which renders it so useful for certain purposes, for instance for transmitting steam and the mechanical force by flexible tubes.

* Incorrectly, we believe; the discovery is really due to Mr. Chs. Goodyear of New York, U.S.—W. F.

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The principal conditions of success in this manufacturing operation had been carefully determined; in England, America and France, several methods had been successively imagined, which realized more or less perfectly the curious and important modifications of the sulphated substance; but it was not known in what the chemical reaction consisted; no one had an accurate idea of what is termed *desulphuration*. Lastly, it was impossible to understand, and consequently to prevent, certain alterations, especially the rigidity and fragility of several objects, after having served often but a short time the purposes for which they were made.

The investigations which I have the honour to bring before the Academy have had for their object to throw some light on these points of applied science. I shall first describe what takes place in one of the processes of vulcanization still employed by several manufacturers; it will then be more easy for me to point out the effects of other processes. If a strip of caoutchouc from 2 to 3 millims. thick is kept immersed for two or three hours in melted sulphur at the temperature of 234°–240°, the liquid will penetrate into the pores like water or alcohol, as we have already shown, but still more quickly, and the weight of the strip will have increased by 10- to 15-hundredths. The organic matter will have experienced no considerable modification in its properties; it can be shaped, and its recent sections joined, just as in the normal state; solvents will act upon it with the same force; but its porosity will be diminished. If the temperature be now raised to 275°, 302° or 320°, in any medium whatever, inert of itself, a few minutes suffice to effect the change. By prolonging the action of the temperature, the object in view would be exceeded, the product, gradually less supple and less elastic, would soon become hard and fragile. This last alteration would be still more marked if the caoutchouc were kept at the above temperatures, 275°–320°, in melted sulphur. The amount absorbed would gradually increase until it became in twenty-four hours, for instance, nearly equal to the weight of the organic matter, or forming 48 per cent. of the stable compound.

From the commencement of the reaction of the sulphur at this temperature, and during the whole of the time it is continued, a slight but constant disengagement of sulphuretted hydrogen takes place*. Even the liquid sulphur at 302° absorbs, and is capable of retaining a volume of this gas nearly equal to its own. A curious phænomenon results from this fact; at the moment when the sulphur crystallizes, from the decrease of temperature, each crystalline particle liberates a bubble of gas; sometimes this is disengaged; sometimes, meeting with the crystals, it raises them and remains interposed, so that gradually the whole mass rises, and increases from 15 to 20 per cent. of its primitive bulk, instead of diminishing, as would happen in a normal crystallization of pure sulphur.

* At the same time an equivalent quantity of an organic substance separates, which contains more carbon than the caoutchouc, and which can be extracted with a hot solution of caustic potash or soda, which does not act perceptibly upon the mass of caoutchouc combined with the sulphur.

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Instead of causing the liquid sulphur to penetrate at a temperature near its melting-point, the caoutchouc may be mixed by a mechanical roller with from 12 to 20 per cent. of its weight of sulphur in a state of fine powder; the properties of the organic matter are not altered, but can be modelled and joined together as in the normal state. But if the temperature is now raised to the point at which the vulcanization is effected, it takes place as in the first case; the suitable term would be equally exceeded under the same circumstances, and the alterations above mentioned would be likewise manifested.

Composition and Properties of the Caoutchouc vulcanized by the Methods above described.—When the suitable term has not been exceeded, the organic substance contains sulphur in two different states; from 1 to 2 per cent. is held in intimate combination*; the remainder is simply interposed in its pores.

The uncombined excess of sulphur is gradually eliminated from the caoutchouc by the mechanical effect of the extension and contraction of the pores; this continues for several months. Several chemical reagents remove the interposed sulphur more rapidly and more completely, as hot solutions of caustic potash and soda (and even cold in the course of a month if renewed frequently), sulphuret of carbon, essential oil of turpentine, benzine and anhydrous æther. These liquids cause the organic matter to swell to such an extent, that its bulk is soon increased eight or nine times.

Æther removes the sulphur in a peculiar manner. A small proportion is first dissolved, which is then carried to the exterior; there it separates in crystalline particles; other particles, successively dissolved in the interior, follow the same course, and increase the size of the crystals, which soon become pretty large, and are of the octahedral form. Neither turpentine nor benzine transfer the crystalline particles of the sulphur removed from the interior of the swollen mass to the exterior. This peculiarity appeared to me to be owing to the hitherto unobserved greater solvent power of the turpentine and benzine; in order to verify this fact, I saturated these two liquids, kept at a constant temperature of 167° F., in the water-bath with an excess of flowers of sulphur. The yellow solutions were immediately filtered, when they deposited crystals on cooling:—

	In turpentine.	In benzine.
The hot solutions contained	0·0587	0·0733 sulphur.
After cooling they contained	0·0135	0·0173 sulphur.

Moreover, the crystals were not similar; the turpentine, on slow cooling, as also on evaporation at 77°, had deposited the sulphur in small octahedrons; on sudden cooling, it deposited it in acicular prisms; in the benzine the crystals were prismatic. It is curious to observe this last mode of crystallization in a test-tube; a number of diaphanous rectangular plates are seen to form, ascend and descend

* This compound has not altered the relations between the elements of the organic substance which is represented by the formula $C^{8}H^{7}$, as I have proved by several analyses made upon normal caoutchouc, or one of its two unequally soluble parts, and also on the compounds containing from 0·015 to 0·485 sulphur.

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rapidly in the liquid, and successively agglomerate at the bottom of the vessel in laminæ, which thus gradually lengthen; if, after cooling to 59°–60°, evaporation is allowed to recommence, a further crystallization takes place now in diaphanous octahedra, which attach themselves to the extremities of the opake yellowish lamellar prisms first formed. On evaporation with heat, long silky laminæ are obtained. A drop of the same solution in benzine, placed on the object-bearer of the microscope, deposits on evaporation transparent octahedra:—

100 parts of hot sulphuret of carbon dissolve..	73·46 sulphur.
100 parts of cold sulphuret of carbon dissolve	38·70 sulphur.
100 parts of hot æther dissolve	0·54 sulphur.
100 parts of cold æther dissolve	0·188 sulphur.

On cooling, the sulphur crystallizes in large octahedra from sulphuret of carbon; from æther, in minute octahedra and some prisms.

Æther and sulphuret of carbon, kept for a long time in contact with vulcanized india-rubber, retain from 4 to 5 per cent. in solution, which may be isolated by evaporating several times, and each time removing by æther the free sulphur, and then treating with anhydrous alcohol, which removes from 1 to 1·50 per cent. of fatty matter. The caoutchouc thus extracted may be separated into two portions, one very ductile, which dissolves in benzine, and is deposited on evaporation; the other more tenacious, less extensible and insoluble. Both these portions come from the interior of the strips at a certain depth, where the combination is less intimate, and contains less sulphur than near the surface.

The want of homogeneity in the combination of the sulphur with the organic substance is greater in the two other methods of vulcanization, which I shall describe further on.

After vulcanization, the caoutchouc still consists of two parts, differing in cohesive power and solubility. This may be proved by keeping it immersed for two months in a mixture of 10 parts sulphuret of carbon and 1 of absolute alcohol. The dissolved portion consists of the interposed sulphur, which is removed after desiccation by a solution of caustic soda; the organic substance the least aggregated is then left as a translucid, yellowish, slightly-resisting mass. The undissolved portion is become more brown and less transparent. The following are the proportions obtained in the experiment, besides the fatty matter:—

Insoluble tenacious portion.....	65
Soluble soft portion.....	25
Excess of sulphur	10

Vulcanized objects, applied on metals, especially upon silver, gold, copper, lead and iron, act by their interposed sulphur; they sulphurize more or less rapidly the metallic surfaces in contact with them. The washers placed between the flanges of tubes used for transmitting steam under a pressure of 4 or 5 atmospheres, which are exposed consequently to a temperature of 293°–308°, soon lose their elasticity and become hard and brittle, owing to the combination

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which takes place between the free sulphur and the caoutchouc. This is greatly avoided by desulphuration with caustic alkaline solutions, or by the use of a new method of vulcanizing, described at the end of this paper.

Some comparative experiments made with, 1st, *normal*, 2nd, *vulcanized*, 3rd, *desulphurated* caoutchouc, show that, on immersion for two months under similar circumstances, the absorption of pure water was for the first 0·200–0·260, for the second 0·042, and for the third 0·064. Some balloons, 2 millims. in thickness, filled with water, and submitted to a pressure which doubled their diameter, lost by continual transpiration in twenty-four hours, and per square metre, the normal caoutchouc 23 grms., the vulcanized 4 grms. Similar balloons, filled with air under the same pressure, experienced scarcely any loss in eight days. The perceptible loss of water through a thin layer of caoutchouc will be readily understood; the liquid introducing itself by capillary attraction into the pores of the organic substance, and replacing in a continuous manner the quantities which evaporate at the external surfaces. That the air and gases in general do not behave in a similar manner needs no explanation.

The process of cold vulcanizing invented by M. Parkes consists in plunging the sheets or tubes of caoutchouc into a mixture of 100 parts sulphuret of carbon and 2·5 parts protochloride of sulphur; the liquid, penetrating into the organic substance, causes it to swell, and deposits sulphur, which unites with the caoutchouc, owing to the decomposition of the unstable compound which it formed with the chlorine. The superficial parts would be too strongly vulcanized, and would become brittle, if care were not taken to remove the objects after a minute or two, and to immerse them immediately in water, as recommended by M. Gérard. The chloride of sulphur is decomposed by its contact with water, while the portions which have penetrated further continue their sulphurizing action in the interior. This is an ingenious plan of regulating this kind of cold vulcanization.

Another process, which appears preferable on account of the salubrity and regularity of the operation, is due to the same inventor; it consists of immersing in a closed vessel for three hours the objects to be vulcanized, in a solution of polysulphuret of potassium indicating 25° Beaumé, at a temperature of 284°, and then washing in an alkaline solution, and afterwards in pure water. In this manner the useful amount of sulphur is combined with the caoutchouc without an excess being left in its pores; and we thus avoid the inconveniences which result from the unequal sulphurization of the organic substance.—*Comptes Rendus*, March 29, 1852.

On the alleged Adulteration of Pale Ales by Strychnine.
By Professors GRAHAM *and* HOFMANN.

Having undertaken, at the request of Mr. Allsopp, an inquiry into the purity of bitter beer, with particular reference to its alleged

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adulteration by strychnine, we now submit the results which we have obtained upon the subject :—

Strychnine, the alleged substitute for the hop, is a fine crystallizable substance, extracted from *nux vomica*, and belonging to the class of vegetable principles termed alkaloids, of which quinine from Peruvian bark and morphine from opium are the most familiar examples. These substances, although susceptible of the most valuable medical application in small doses, are, generally speaking, remarkable for their energy as poisons, and for the intense bitterness of their taste, two properties which are developed in strychnine in the highest degree. Half a grain of the latter substance would poison, and the bitterness of the same minute quantity is perceptible in every drop of 6 or 8 gallons of water in which it is dissolved.

It may be stated at once, that the quantity of strychnine which we find necessary to impart to beer the degree of bitterness possessed by pale ales is, for a gallon of beer, 1 gr. of strychnine, or double the fatal dose. The price of strychnine is about 16*s.* the ounce, which does not amount to so much as one penny per grain. Estimating the annual production of pale ale in Burton at 200,000 barrels, the strychnine required as a bitter would however amount to 16,448 oz , and cost £13,158 ; while nobody believes that so much as 1000 oz. of strychnine are annually manufactured over the whole world. The bitterness obtained by means of strychnine is equal in degree to that of the hop, but very different in kind, and easily distinguished when the two bitters are compared. The bitter of the hop is immediate in its action upon the palate, is accompanied by a fragrant aroma, and soon passes off, whilst that of strychnine is not so instantaneous ; but when the impression is once communicated, it is more lasting, and becomes, from its persistence, like that of a metallic salt. The bitter of strychnine is indeed easily distinguishable from that of the hop when deliberately tasted.

Still it would be highly desirable to be able to identify strychnine in beer by the actual extraction of the substance, and the application to it of a chemical test of absolute certainty. Fortunately those poisons which have the most violent action upon the animal œconomy possess often also the best marked reactions, or their physiological and chemical properties are equally salient. Thus arsenic and hydrocyanic acid are the most easily detected of chemical substances, and strychnine proves to be not far behind them in this respect.

A quantity of strychnine, not exceeding one-thousandth part of a grain, is tested and recognised to be strychnine in the following manner :—The powder is moistened with a single drop of undiluted sulphuric acid, and a small fragment of chromate of potash placed in the liquid*. A beautiful and most intense violet tint immediately appears at the points of contact, and is speedily diffused over the whole liquid. Although most intense, the colour disappears entirely in a few minutes. The admixture of the smallest quantity of organic matter, however, interferes with the success of the process.

* Marchand's test as modified by Dr. Otto. See Chem. Gaz., vol. v. p. 15.—W.F.

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In order to apply the test, in operating upon a complex liquid like beer, the strychnine must first be extracted from the liquid, and obtained in a pure or nearly pure condition. This difficulty, which appears at first considerable, may be readily surmounted, and the strychnine, if it really exist in beer, be separated, and its nature established in the most certain manner.

For this purpose, 2 oz. of ivory-black, or animal charcoal, were shaken in half a gallon of beer to which half a grain of strychnine had been purposely added. After standing over night, the liquid was found to be nearly deprived of all bitterness, the strychnine being absorbed by the charcoal. The liquid was now passed through a paper-filter, upon which the charcoal containing the strychnine was collected and drained.

The next step was to separate the strychnine from the charcoal. This was readily effected by boiling the mixture for half an hour in 8 oz. of ordinary spirits of wine, avoiding loss of alcohol by evaporation. The spirits, which now contained the strychnine, were next filtered, and afterwards submitted to distillation. A watery fluid remained behind, holding the strychnine in solution, but not sufficiently pure for the test. The final purification was accomplished by adding a few drops of potash to the watery fluid, and then shaking it with an ounce of æther. A portion of the ætherial solution, evaporated upon a watch-glass, left a whitish solid matter of intense bitterness; and this was recognised to be strychnine by giving the violet tint previously described upon the application to it of sulphuric acid and chromate of potash.

Having satisfied ourselves, by repeated experiments with samples of beer to which strychnine had been previously added, of the never-failing efficiency of the above method of extraction, we now proceeded to the actual examination of the commercial article. With this object, a series of samples were taken indiscriminately from the stores of a considerable number of the London bottlers who supply the public with Allsopp's pale ale. With few exceptions, the casks from which the samples were taken had all been received in London before the 20th of March, *i. e.* the period, when the possible use of strychnine in the manufacture of bitter beer was first brought before the English public.

Not one of these varieties of beer, when tested with the greatest scrupulousness, gave the slightest evidence of the presence of strychnine.

Were mere bitters all that is required, it would be easy to prove that the extract of quassia would supply a bitter which is perfectly harmless and agreeable, and infinitely less expensive than strychnine. Strychnine could not fail to be rejected, from the ungrateful metallic character of its bitterness, independent of all objections of a more serious kind. This peculiarity of taste is also calculated to betray its presence. Small too as the proportion of strychnine may be which is necessary to impart the degree of bitterness to pale ale, the quantity rises, as has been seen, to a poisonous dose in half a gallon of the fluid; and as this poison is one of those which are known to accumulate in the system, its poisonous action would ine-

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vitably follow, in occasional cases, upon the consumption of much smaller portions of beer when continued for many days without intermission. The violent tetanic symptoms of poisoning by strychnine are also such as could scarcely fail to excite suspicion and alarm. Add to these disadvantages the certainty of the means of detecting strychnine in beer by the chemical tests described above, which any medical man or practical chemist can apply, and the chance of the use of so dangerous a substance for any purpose of adulteration becomes in the last degree improbable.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

April 5th, 1852. (Col. Philip Yorke, Vice-President, in the Chair.) The following paper was read:—

"On the Detection and Qualitative Separation of Tin, Antimony and Arsenic, and on the Relation existing between these Metals and others which are precipitated from their acid solutions by Sulphuretted Hydrogen," by Charles L. Bloxam.

After a few prefatory remarks, and a review of the principal methods hitherto proposed for effecting the object in view, the author proceeded to describe the method which he has been led to adopt, which consists in treating the precipitated sulphurets of arsenic, antimony, and tin with solution of sesquicarbonate of ammonia, which dissolves the sulphuret of arsenic and part of the sulphuret of tin; the arsenic is detected in the precipitate, thrown down from the solution by hydrochloric acid, by the test of Fresenius and Bobo, whilst the tin is sought for in another portion of the same precipitate, by deflagrating it with nitre, precipitating the aqueous solution of the fused mass with nitric acid, reducing the tin from the precipitate by fusion with cyanide of potassium, treating the reduced metal with hydrochloric acid, and testing the solution for protochloride of tin with perchloride of mercury. Antimony and tin are detected in the precipitate left undissolved by sesquicarbonate of ammonia; this precipitate is dissolved in nitro-hydrochloric acid, and the solution boiled with excess of sesquicarbonate of ammonia, when the whole of the tin is precipitated, and part of the antimony remains in solution; the tin may be discovered by reducing the precipitate as above described, and the antimony may be precipitated as sulphuret by acidulating the solution with hydrochloric acid, and passing sulphuretted hydrogen.

Some curious facts were stated respecting the insolubility of bisulphurets of tin in sulphuret of ammonium, in the presence of sulphuret of copper and tin. Methods were described by which these difficulties may be overcome.

All the processes mentioned in the paper were verified by experiments upon mixtures containing known quantities of the various metals.

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THE CHEMICAL GAZETTE.

No. CCXXXI.—June 1, 1852.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Bismæthyle (Bismuth-æthyle), a new Organic Radical containing Bismuth. *By* D. Breed, M.D., New York.

Bismuth is allied in many respects, particularly in its combining proportions, to antimony; but it differs from that substance in the insolubility of its sulphur compounds in sulphuret of ammonium, and as yet we have not been able to combine it with hydrogen.

After the discovery of stibæthyle*, Prof. Löwig sought to ascertain whether bismuth may not form compounds with æthyle and methyle similar to those of antimony, and in fact, as already stated in the treatise upon stibæthyle, bismæthyle was produced quite agreeing in its external properties with stibæthyle.

During my residence in Zürich in the summer of 1851, under the instruction of Prof. Löwig, I submitted bismæthyle to a particular investigation; but I regret my stay was not long enough to bring the research to a termination. In the following pages I give the results thus far obtained, and hope in a second article to complete the details of the investigation.

The substances for producing bismæthyle are iodide of æthyle and bismuth-potassium. The latter is produced similarly to antimonium-potassium; but as bismuth fuses easier than antimony, we must, in the preparation of bismuth-potassium, be careful that the process progresses as fast as possible. Bismuth-potassium is best obtained when we bring 16 oz. finely-pulverized bismuth and 20 oz. crude tartrate of potash (also pulverized) into a Hessian crucible, which is then covered, and at first slowly heated; then the fire is increased to such a degree that the crucible attains to white heat in half an hour at the longest. In this state the furnace, yet full of glowing coals, is closed air-tight, and left to cool slowly. The bismuth-potassium is found at the bottom of the crucible as a silver-white leafy crystalline mass. It is easily fusible, and often remains fluid or soft after cooling. Brought in contact with water, it evolves hydrogen gas. It tastes strongly alkaline. Exposed to the air, it soon decomposes; but in thick pieces it can be kept long in a closely-stopped bottle. The alloy is brittle and easily pulverized.

* The investigations of Profs. Löwig and Schweizer on Stibæthyle will be found at pp. 201, 372, vol. viii.; those of Landolt on Stibmethyle, at p. 181, vol. ix.—Ed. *Chem. Gaz.*

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The iodide of æthyle is produced in the ordinary way by the united action of iodine and phosphorus upon alcohol of 0·833.

Bismæthyle differs from stibæthyle essentially in the fact that it cannot be distilled alone, but at a certain temperature decomposes with a powerful explosion. From this it is evident that it cannot be formed by heating iodide of æthyle with bismuth-potassium, as stibæthyle is formed with antimonium-potassium. The best method of making bismæthyle is the following:—Finely-pulverized bismuth-potassium is quickly brought into a small flask into which an excess of iodide of æthyle is speedily poured; the apparatus is immediately closed with a cork, through which passes a long distillation-tube discharging into a receiver cooled by ice. After a few moments, the action of the iodide of æthyle upon the bismuth-potassium commences, accompanied by considerable evolution of heat, in consequence of which the excess of iodide of æthyle which has been added distils off. Cautious exposure to the water-bath is sometimes employed to facilitate the complete distillation, or to hasten the commencement of the action. We now pour distilled and well-boiled water into the flask, close it air-tight, and then leave it upon the water-bath until the mass softens and the iodide of potassium is dissolved. We now repeat the described operations with ten or twelve flasks, and then bring their softened contents as quickly as possible into a large flask filled with carbonic acid, and repeatedly shake the whole with a considerable quantity of æther, which must not be sparingly used, since bismæthyle is only slightly soluble in æther. To the ætherial solution we add water freed from air, and completely distil off the æther over the water-bath. After this operation is terminated, we find the bismæthyle below the water upon the bottom of the flask. To obtain it completely pure, it is distilled with water over a spirit-lamp, then shaken with a small portion of dilute nitric acid to remove a little oxide which forms, and finally dried over chloride of calcium. It is evident that in all these operations the air must be excluded. I employed the apparatus of Profs. Löwig and Schweizer, described in the treatise upon stibæthyle.

The analysis of bismæthyle offers on the whole no difficulty. The combustion is easy and complete with oxide of copper itself, without the employment of chlorate of potash. The determination of the bismuth is also easy, because it may be completely oxidized by nitric acid. It is best accomplished in the following manner:—Into a capacious flask we bring a little water, and into this the glass bulbs filled with weighed bismæthyle. The flask is closed with a cork, through which passes a cup-tube drawn to a point below, and dipping into the water of the flask. Through this cup-tube fuming nitric acid is added. When all is arranged, the small bulbs filled with bismæthyle are broken by shaking, and afterwards the bismæthyle is decomposed by nitric acid. After the oxidation, the whole apparatus without separation is left some time standing, then the nitric acid solution is poured into a weighed platinum dish, and the wash-water of the flask and cup-tube added. We now evaporate to

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dryness upon the water-bath, and cautiously decompose the nitrate of bismuth over a spirit-lamp, and weigh the oxide of bismuth thus obtained. Below are the results of a few analyses:—

Carbon	24·81	24·38	24·27
Hydrogen	5·24	5·27	5·26
Bismuth.....	69·95	70·47	70·47

If we assume for the atomic weight of bismuth 208, as given by the latest researches, the accompanying analyses best agree with the following atomic proportions:—

12 atoms carbon	72	24·44
15 atoms hydrogen	15	5·08
1 atom bismuth	208	70·48

The formula for bismæthyle therefore completely corresponds to that of stibæthyle, $BiAe^3$.

Bismæthyle appears as a watery, clear or pale yellow, thin-flowing fluid, of 1·82 spec. grav. It possesses an extremely disagreeable odour, resembling stibæthyle, and produces, even when only a trace is inhaled, a highly disgusting burning sensation upon the tip of the tongue. In the air it throws up thick fumes, inflames with a slight explosion, diffusing a deep yellow smoke of oxide of bismuth. This appearance is most brilliant if we expose to the air some filter-paper covered with bismæthyle. By fuming nitric acid it is decomposed with vivid appearance of fire and violent explosion. In the same manner it burns in chlorine gas, whilst carbon is deposited. In contact with bromine it burns, and shows throughout the same appearances as stibæthyle. It is quite insoluble in water, not easily soluble in æther, but easily so in anhydrous alcohol. If bismæthyle be heated by itself in a retort, it commences to boil even below 50°, evolving a gas which burns with a clear flame and contains no bismuth, but metallic bismuth is deposited in the retort. If we raise the heat to 360°, then the whole apparatus is instantaneously shattered by a violent explosion.

In chemical relations, bismæthyle behaves quite like an organic radical. If to its alcoholic solution we add a solution of iodine or bromine, the colour vanishes under considerable evolution of heat and production of iodide or bromide of bismæthyle. The compounds however are less permanent than the corresponding ones of stibæthyle. If, for example, we leave standing for a short time an alcoholic solution of iodide of bismæthyle, iodide of bismuth is deposited. Bismæthyle easily dissolves in dilute nitric acid, and of course the solution contains nitrate of bismæthyle; if however we evaporate the nitric acid solution, pure nitrate of bismuth remains.

The description of the compounds of bismæthyle must be reserved for a second paper.—Silliman's *Journal*, May 1852.

On the Preparation of pure Hydrate of Potash and Carbonate of Potash. *By* Henry Wurtz, A.M.

In preparing pure potash compounds, it is highly necessary, especially in order to avoid the possibility of the presence of soda, to

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select, as a starting-point, some compound of potash which differs considerably in solubility from the corresponding soda compound. Either the bitartrate or the sulphate, therefore, is usually preferred.

The bitartrate is ignited, the carbonaceous mass washed with water, and the solution of carbonate of potash thus obtained diluted and boiled with slack lime in the usual way in an iron kettle; the solution of hydrate of potash thus obtained is boiled to dryness, and the alcoholic solution of the residue evaporated in silver dishes, to obtain what is denominated *alcoholic potash*. This product should be, and most usually is, entirely free from sulphate of potash and chloride of potassium, since it is easy to crystallize the bitartrate free from these salts.

But an almost invariable accompaniment of this alcoholic potash is a trace of silicate of potash. The solution may assume no cloudiness on the addition of solution of hydrochlorate of ammonia, or upon addition of an excess of hydrochloric acid, and afterwards an excess of ammonia; but on adding excess of hydrochloric acid, and evaporation to dryness in a platinum capsule, the aqueous solution of the residue will be found to have flakes of silica floating in it. Very few specimens that I have met with have stood this test. It is to be inferred that the soluble silicates of potash are not wholly insoluble in alcohol; but a question arises concerning the source from whence the silica is so frequently derived. It may be from the lime used in some cases, or from silicium contained in the iron of the kettles employed. I am enabled to state, in addition, that of many specimens of commercial *carbonate of potash* which I have examined, some of which purported to have been prepared from cream of tartar by the method above alluded to, none have been found entirely free from silica. I have even found traces of this impurity in crystals of commercial *bicarbonate of potash*.

This constant contamination of potash and carbonate of potash with silica being a very important matter, in consideration of the frequent use of these two substances in chemical analysis, I have been induced to devise a means of separating the silica from the carbonate. This I have accomplished by the use of carbonate of ammonia.

An aqueous solution of the carbonate which is to be freed from silica is evaporated to dryness on the sand-bath (best in a sheet-iron dish), adding from time to time lumps of carbonate of ammonia. The silicate is thus converted into carbonate; and on dissolving the residue of the evaporation in water, the silica appears in the form of flakes floating in the liquid, and may be separated by filtration. This solution of carbonate of potash, free from silica, may now be used for the preparation of pure hydrate of potash, taking care to use lime which is also free from silica.

I may here introduce a few words with regard to the preservation of hydrate of potash for use in analysis. Its preservation in the solid form is evidently no difficult matter; but when we attempt to keep the solution in glass bottles for the sake of convenience in using it as a reagent, we generally find that it very soon takes up

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silica from the glass. I have found, however, that flint-glass bottles will preserve such a solution much longer than any other, lead-glass not being easily acted upon, probably because it contains very much less silica. It might not be useless to make a trial of bottles made of thin soft iron or sheet iron for this purpose; but it is probable that pure *silver* is the true material for bottles in which solution of potash is to be preserved. A very thin shell of silver might first be made, and afterwards strengthened by coating it thickly with galvanic copper.

The ease with which sulphate of potash can be obtained in a state of purity has long ago suggested its use as a material from which to prepare pure potash. Schubert* proposed to treat pulverized pure sulphate of potash with a concentrated solution of pure baryta, the latter somewhat in excess; and during the evaporation of the solution of hydrate of potash thus obtained, the excess of the baryta is precipitated by the carbonic acid of the air. This however appears to be a very expensive process. I have devised another method of treating pure sulphate of potash, so as to obtain pure hydrate of potash therefrom; it consists merely in operating upon the sulphate of potash in a manner similar to that in which sulphate of baryta is operated upon to procure hydrate of baryta, that is, in converting the sulphate into sulphuret by the conjoined application of a reducing agent and a red heat, and to decompose the aqueous solution of the sulphuret by the action of an oxide of a metal whose sulphuret is insoluble, such as oxide of iron (?), oxide of copper or deutoxide of manganese. I use as a reducing agent, instead of charcoal, oil, resin, &c., *coal-gas*. This application of coal-gas was proposed by Dr. Wolcott Gibbs. If it is found that the decomposition is not perfect, and that the solution of sulphuret of potassium contains some sulphate of potash, or if a little sulphate is formed in the solution by oxidation, it is removed by the introduction of a little solution of baryta, according to the method of Schubert. I am not yet prepared, however, to give the details of this method.—*New York Journ. of Pharm.*, February 1852.

On the Preparation of chemically-pure Hydrate and Carbonate of Soda. By Henry Wurtz, A.M.

The remarks made in the last article with reference to the presence of silica in alcoholic potash, apply also, though not so generally, to commercial alcoholic soda. Few specimens of this product are met with which are so free from silica that it cannot be detected by saturation with hydrochloric acid, evaporation to dryness in a platinum vessel and resolution in water. Whatever may be the origin of the silica in this case, it is very often present.

I have selected, as the most convenient substance from which to prepare pure hydrate and carbonate of soda, a product which occurs very abundantly in commerce under the name of "carbonate of soda." It is in the form of a very fine white powder, and on ex-

* Journ. für Prakt. Chem., xxvi. 117.

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amination turns out to be the ordinary monohydrated *bicarbonate* of soda, $NaO,2CO^2+HO$; for upon ignition 7·756 grs. lost 2·7595 grs. of carbonic acid and water, which is equal to 35·60 per cent.; bicarbonate of soda should lose 36·88 per cent. It may be mentioned, on this occasion, that a preparation sent over here by Button, a London pharmaceutist, under the appellation of "chemically-pure carbonate of soda," upon examination turned out to be also *bicarbonate*. 2·324 grs. lost by ignition, 0·845 gr.=36·45 per cent.

The commercial bicarbonate above mentioned contains of course all the impurities of the carbonate from which it is made, this being an inevitable consequence of the method by which it is manufactured, which, as described in Knapp's 'Chemical Technology,' is simply to expose commercial crystals of carbonate of soda to the action of carbonic acid gas, which it takes up to the extent of 1 equiv., falling into a fine powder, with evolution of heat and loss of water of crystallization. These impurities, in the case of the specimen operated upon by me, were, besides a considerable amount of silica, sulphate of soda, chloride of sodium, a trace of phosphoric acid detected by molybdate of ammonia, and a little organic matter which imparted to the mass a soapy smell.

The sulphate, phosphate, and chloride are easily removed by washing with water by decantation, with a loss however of at least one-half of the material. When the washings, after addition of excess of nitric acid, no longer react with nitrate of silver or with chloride of barium, the mass is introduced into porcelain dishes, and dried on the sand-bath; when dry, it is exposed to a high sand-bath heat, though not to a red heat, for two or three hours. By this treatment, not only are 1 equiv. of carbonic acid and 1 equiv. of water expelled, but the greater part or the whole of the silicate is decomposed and converted into carbonate, so that a solution of the mass in water will now be found full of flakes of silica.

The filtered solution should now be tested for silica; and if not yet entirely free from it, must be evaporated again to dryness, with addition of lumps of carbonate of ammonia, exactly as proposed by me in the last article, to separate silica from carbonate of potash. The residue of this last evaporation, on solution in water, filtration, and evaporation in platinum, silver, or even clean sheet-iron (never in glass or porcelain) dishes, will give pure carbonate of soda, from which may be prepared the pure hydrate of soda, observing the precaution of using lime which is free from silica.—*New York Journal of Pharmacy*, February 1852.

On some Products from the Essential Oil of Turpentine.
By J. CHAUTARD.

In a former note*, I described the action of the hypochlorite of lime upon the essential oil of turpentine; the product obtained is identical in properties and composition with the chloroform prepared

* Chem. Gaz., p. 68 of the present volume.

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from alcohol. The following is a brief account of the results to which my further researches have led:—

1. The reaction which I obtained with the hypochlorite of lime and the essential oil of turpentine is repeated with the same appearances, and furnishes chloroform when the essential oils of peppermint, juniper, copaiba, lavender, lemon, thyme, rue, savine, valerian, rosemary and bergamot are treated in an analogous manner.

2. A mixture of 100 parts of hydrochloric acid, 25 of deutoxide of manganese, and 6 of turpentine, when distilled, agitating from time to time until ebullition has commenced, gives an acid water, and a yellow viscid liquid heavier than water, and of a slightly aromatic odour. During the reaction, no free chlorine is disengaged; all these reagents appear to enter into combination with the oil. On attempting to distil this product in order to obtain it pure, it is decomposed with phænomena closely analogous to those which are exhibited in the distillation of the chloride of the oil $C^{20} H^{12} Cl^4$, obtained by M. Deville. The boiling-point rises rapidly to 464° F. Some fumes of hydrochloric acid are disengaged, which increase in proportion as the thermometer ascends; they were so copious at 518°, that I was compelled to stop the operation. A thick black liquid remained in the retort, which solidified on cooling. What is remarkable in the distillation of this liquid is the change of colour which it undergoes in the different phases of the operation, passing through yellow, green, blue, indigo and brownish-black. The want of homogeneity of this substance prevented me from submitting it to analysis; but everything leads me to believe that it is identical with the chloride of the oil obtained directly by the action of free chlorine upon the essential oil of turpentine.

3. Hypobromite of lime furnished by its action on the oil of turpentine a product perfectly parallel to that which the hypochlorite yielded. Some slaked lime is mixed with water, so as to form a perfectly homogeneous semi-fluid paste; bromine is gradually added, with constant agitation, until the peculiar colour of this body ceases to disappear. The mass becomes heated during the operation and thickens; sufficient water is then added to restore it to its primitive consistence. When this is done, oil of turpentine is poured into the mixture in quantity equal to half the lime employed, and the whole well agitated so as to cause a perfect emulsion. The mixture is then introduced into a retort and heated; a lively reaction ensues, carbonic acid is disengaged, and a heavy liquid of an ætherial odour distils over along with some water. This crude product is rectified by several fractional distillations, when a liquid is obtained, the properties of which exhibit the greatest analogy with those of common bromoform.

4. Some experiments made upon other essential oils gave similar results to the preceding; this leads me to think that bromoform, as also chloroform, are constant products of the action of the hypobromites and of the hypochlorites upon all the essential oils.—*Comptes Rendus*, March 29, 1852.

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Examination of the Bark of **Cinchona regia.** ***By*** **R. Schwartz.**

Yellow bark, which is said to be procured from *Cinchona lancifolia*, Mutis, contains two bases, cinchonine and quinine, and three acids, kinic, cinchotannic and kinovic acids. It is of a peculiar red colour from the presence of cinchona-red, a product of decomposition of the cinchotannic acid. Cinchonine and quinine, as also kinic acid, have often formed the subject of investigations, with the view of determining their composition; but nothing is at present known regarding the composition of cinchotannic acid and the cinchona-red.

When the bruised bark is boiled with water, all the above substances can be detected in the aqueous extract. By repeated boiling with water, the kinic and cinchotannic acids may be completely removed from the bark, but not so the cinchona-red and the kinovic acid, the greater part of both of which substances remains undissolved in the bark.

When the bark, after exhaustion with water, is boiled with thin milk of lime, the whole of the kinovic acid is dissolved by the lime, whilst the cinchona-red remains in the bark. But if the bark, after exhaustion with water, be treated with alcohol containing muriatic acid, the whole of the kinovic acid becomes dissolved; and the cinchona-red, which is separated from its combinations by the muriatic acid, dissolves in the alcohol, which thereby acquires a red colour.

Kinovic acid exists in but very small quantity in the aqueous decoction of the bark; the greater part remains in the bark which has been exhausted with boiling water. Hence the kinovic acid exists in this bark, at least the greater part, in the free state, as it is almost perfectly insoluble in water. On boiling bark which has been freed by water from all soluble parts with thin milk of lime, and filtering the decoction thus procured, a yellowish liquid is obtained, in which the addition of muriatic acid causes a copious precipitate of kinovic acid in the form of gelatinous flakes. In this way we obtain from the genuine cinchona barks a quantity of kinovic acid, which is not less than that which may be obtained in the same manner from the bark of the *Cinchona nova*.

To procure the kinovic acid in a pure state, its lime salt dissolved in water is treated with animal charcoal, and the filtered liquid decolorized by the charcoal is decomposed with muriatic acid. The gelatinous precipitate was washed with water until the wash-water ceased to be troubled by solution of nitrate of silver. The acid thus obtained, and dried at 212° F., yielded—

Carbon	68·90	68·80	12 =	72	68·57
Hydrogen	8·85	8·87	9	9	8·57
Oxygen	22·25	22·33	3	24	22·86
	100·00	100·00			100·00

All the properties of the substance thus obtained, as also its composition, satisfactorily show the identity of this bitter substance with the kinovic acid or the so-called kinova-bitter, which exists ready formed in the bark, and may be artificially obtained from caincic

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acid (from the bark of the root of *Chiococca racemosa*). The statements of Winckler regarding the occurrence of kinovic acid in the genuine cinchona barks are thus confirmed.

Cinchotannic Acid.—The first experiments to obtain this acid in the pure state were made by Berzelius. In the course of the author's investigations, these experiments were repeated, and it was found advantageous to avoid the use of magnesia. The properties of cinchotannic acid given by Berzelius agree perfectly with those observed by the author in this substance. The principal difficulty to be overcome in the examination of this acid is its tendency to absorb oxygen, so that it is hardly possible to obtain the acid without its having absorbed a certain amount of oxygen. There is scarcely any substance which combines so rapidly with the oxygen of the air as the tannic acid of the cinchona barks. This property of absorbing oxygen occurs in a still greater degree in the compounds of the tannic acid with the alkalies and alkaline earths when in the moist state; so that the alkaline cinchotannates, like the pyrogallates, might be used in eudiometric experiments. The bark contains but a small quantity of cinchotannic acid; that required for the author's experiments had to be obtained from 48 lbs.

The bruised cinchona bark was boiled with water, strained through linen, and treated with some calcined magnesia, which took up some cinchona-red, and became reddish-brown. The filtered liquid gave with acetate of lead a copious brownish-red precipitate, which was decomposed in water by sulphuretted hydrogen. The liquid filtered from the sulphuret of lead, when mixed with tribasic acetate of lead, yielded a brownish-red precipitate, which was dissolved in acetic acid; a great part of it then remained undissolved. In this process the kinovic acid with cinchona-red remain with the sulphuret of lead. The greater part of the cinchona-red remains undissolved in combination with some oxide of lead, on treatment with acetic acid. The acetic solution, when treated with ammonia, gives a beautiful pale yellow precipitate, which was washed with water, and then decomposed by a current of sulphuretted hydrogen. The liquid filtered from the sulphuret of lead, which is now entirely free from gum, was freed from a little sulphuretted hydrogen by some alcoholic solution of acetate of lead, and the sulphuret of lead separated by filtration. The further addition of an alcoholic solution of acetate of lead produces a pale yellow precipitate, which when filtered off was washed with alcohol, and placed *in vacuo* over sulphuric acid. At the same time, to prevent oxidation from the small quantity of atmospheric air remaining after the exhaustion, a pasty mixture of protosulphate of iron and hydrate of potash was placed in the globe. On analysis this salt gave the following results:—

Carbon	55·70	28 =	168	55·81
Hydrogen.....	4·60	13	13	4·31
Oxygen.....	39·70	15	120	39·88
	100·00		301	100·00

Hence the composition of this lead salt is expressed tolerably by the

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formula $C^{28} H^{13} O^{15} + 3PbO$. This formula may be regarded as composed of $(C^{14} H^6 O^7, 2PbO) + (C^{14} H^6 O^7, PbO, HO)$.

If we conceive the oxide of lead in this salt to be replaced by equivalent quantities of water, we obtain for the composition of the hydrate of cinchotannic acid, $C^{14} H^6 O^7 + 2HO = C^{14} H^8 O^9$.

To procure the hydrate of cinchotannic acid, pure cinchotannate of lead is decomposed in water with sulphuretted hydrogen. The liquid filtered from the sulphuret of lead is allowed to evaporate over sulphuric acid with a moistened mixture of protosulphate of iron and hydrate of potash. There remained after evaporation a puffed-up, pulverulent, yellow, strongly hygroscopic substance, which became electrical by friction, and had an astringent, somewhat acid taste. As the following analysis shows, the acid had absorbed a certain amount of oxygen during the brief period it came into contact with the air on renewing the sulphuric acid under the bell-glass of the air-pump, whilst part of it still remained unaltered:—

Carbon.....	44·75	42 =	252	44·84
Hydrogen.....	5·49	30	30	5·33
Oxygen.....	49·76	35	280	49·83
	100·00		562	100·00

The formula $C^{42} H^{30} O^{35}$ may be resolved into $2(C^{14} H^{10} O^{12}) + C^{14} H^{10} O^{11}$. Hence two-thirds of the tannic acid had absorbed oxygen, whilst one-third remained unchanged. The formula $C^{14} H^{10} O^{11}$ is $= C^{14} H^6 O^7 + 2HO + 2Aq$. It was attempted to remove these last 2 equivs. of water, which could not be expelled from the hydrate of cinchotannic acid *in vacuo*, by heating the acid to 212° F. in a current of carbonic acid gas. The dark red colour which the substance acquired showed that decomposition had thus been produced, which was confirmed by its partial solubility only in water, and its remaining as a reddish-brown resinous mass. If an aqueous solution of cinchotannic acid be mixed with sulphuric acid, the acid, as shown by Berzelius, is precipitated. If a concentrated aqueous solution of cinchotannic acid be mixed with some muriatic acid and the liquid be heated to boiling, the tannic acid is completely decomposed, and a beautiful red product of decomposition separates in flakes, which dissolve in alkaline liquids with a leek-green colour.

When cinchotannic acid is subjected to destructive distillation, an extremely slight odour of carbolic acid is evolved. The distillate, diluted with water, gives all the reactions which characterize phenylic acid, according to R. Wagner; thus a dilute solution of perchloride of iron produces a beautiful green colour without any precipitate, and on the addition of ammonia this passes into red. This aqueous solution, on the addition of an alkali, absorbs oxygen with great eagerness from the air. If phenylic acid is really produced during the dry distillation of cinchotannic acid, which must be positively determined by further experiments, this would indicate a close relation between the constitution of cinchotannic and kinic

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acids, the latter of which, according to Wöhler's investigations, yields carbolic acid as well as other products. A compound of pure cinchotannic acid with oxide of lead was dried *in vacuo* at 212° F. The analysis of this compound yielded—

Carbon	47·92	12 =	72	47·67
Hydrogen	4·85	7	7	4·63
Oxygen	47·23	9	72	47·70
	100·00		151	100·00

An aqueous solution of pure cinchotannic acid, after exposure to the air, became turbid on the addition of water, and a reddish-brown substance separated, which, when washed with water and dried at 212° F., yielded the following composition:—

Carbon	55·35	36 =	216	55·38
Hydrogen	5·68	22	22	5·64
Oxygen	38·97	19	152	38·98
	100·00		390	100·00

The formula $C^{36}H^{22}O^{19}$ may be resolved into $3(C^{12}H^{7}O^{6})+HO$. On the addition of sulphuric acid to the aqueous liquid after filtration from the above-described body, a red precipitate was produced, which much resembled the former, and was readily soluble in alcohol, but little in water, and when dried at 212° F. yielded—

Carbon	38·87	12 =	72	38·91
Hydrogen	4·81	9	9	4·86
Oxygen	56·32	13	104	56·23
	100·00		185	100·00

This substance may be regarded as a hydrate, $C^{12}H^{9}O^{13}=C^{12}H^{7}O^{11}+2HO$. According to this view, there exist three compounds, which contain 6, 9 and 11 equivs. of oxygen to 12 equivs. of carbon and 7 of hydrogen, as shown by the following formulæ:—

$$3(C^{12}H^{7}O^{6})+HO.$$
$$C^{12}H^{7}O^{9}.$$
$$C^{12}H^{7}O^{11}+2HO.$$

If the composition of the hydrate of cinchotannic acid be expressed by $C^{14}H^{8}O^{9}$, and the formula of that product of oxidation containing least oxygen, $=C^{12}H^{7}O^{6}$, be deducted from this, the formula of anhydrous formic acid is left. Hence if the equivalent of cinchotannic acid unites with 2 equivs. of oxygen, it may yield 1 equiv. of water, 2 equivs. of carbonic acid and 1 equiv. of oxygen in the above-described substance, $C^{12}H^{7}O^{11}$. The production of carbonic acid at the same time as cinchona-red has already been pointed out by Berzelius. The author then passes to the description of the experiments which he made upon the method of procuring, and the composition of the cinchona-red.

Cinchona-red.—Powdered cinchona bark, which had been freed from the substances soluble in water by boiling, was exhausted with

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dilute ammonia; the deep reddish-brown liquid, when treated with excess of muriatic acid, deposited kinovic acid and cinchona-red in voluminous reddish-brown flakes.

These were collected on a filter, washed with water, and heated to boiling with thin milk of lime; the cinchona-red then forms an insoluble compound with the lime, whilst the kinovate of lime is soluble in water. The compound of cinchona-red with lime washed with hot water, was heated with diluted muriatic acid, then placed upon a filter, and washed with water until the filtered liquid ceased to render solution of nitrate of silver turbid. The cinchona-red from which the lime was thus removed was again dissolved in dilute ammonia and reprecipitated by muriatic acid, thoroughly washed with water, dissolved in alcohol, and the solution, filtered from some flakes, evaporated to dryness in a water-bath. The cinchona-red thus obtained, when dry formed a chocolate-brown mass, which was almost insoluble in water, but dissolved readily in large quantity in alcohol, æther and the alkalies, with reproduction of a dark red colour. When dried at 212° F., this substance yielded the following results:—

Carbon	53·63	12 =	72	53·33
Hydrogen	5·36	7	7	5·19
Oxygen	41·01	7	56	41·48
	100·00		135	100·00

The cinchotannic acid must absorb 3 equivs. of oxygen to be able to form 1 equiv. of this cinchona-red 2 equivs. of carbonic acid and 1 equiv. of water. When a solution of cinchotannic acid is treated with a few drops of solution of ammonia, and placed in a glass tube in contact with atmospheric air, the volume of the air is rapidly diminished by the absorption of the oxygen. When the absorption is completed, carbonic acid is evolved on adding a drop of sulphuric acid, and its volume amounts to considerably less than that of the oxygen absorbed; at the same time flakes of a reddish-brown matter, cinchona-red, separate from the liquid. This property of the tannic acid, when combined with a base, of absorbing oxygen, is the cause of the presence of so small a quantity of cinchotannic acid and a comparatively large amount of cinchona-red; and a considerable proportion of this small amount of cinchotannic acid is lost on attempting to separate it, because it mostly passes into cinchona-red, whilst the series of operations requisite to separate it from the other constituents are being carried out.—*Bericht der Acad. d. Wissensch. zu Wien.* June 1851.

Analysis of the Water supplied by the Winchester Water-works Company. By Messrs. THORNTON J. HERAPATH *and* WILLIAM HERAPATH.

The present analysis was undertaken at the request of the Company, by whose permission we publish the result.

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The specimen of water operated upon was taken from the pump at the top of the well, at West Hill, Winchester, on the 5th of September 1851.

The well in question is about 180 feet deep, and penetrates into the chalk.

The water was found, upon analysis, to contain the following substances:—

	Grains per gallon.
Lime	6·9070
Magnesia	0·2706
Potash	minute traces
Soda	2·9312
Oxide of iron	traces
Sulphuric acid	1·3216
Carbonic acid (in combination)	4·9280
Phosphoric acid	minute traces
Chlorine	3·4076
Silicic acid	a little
Organic matter	0·3520

A qualitative analysis induces us to believe that these were combined together as below:—

	Grains per gallon.
Chloride of magnesium	0·240
Chloride of calcium	0·080
Chloride of sodium	5·296
Sulphate of magnesia	0·512
Sulphate of lime	1·440
Sulphate of soda	0·240
Alkaline carbonates?	a little
Carbonate of lime	11·200
Phosphate of lime	minute traces
Silica	a little
Organic matter	0·352
	19·360

The hardness of the water varied between 12°·5 and 13°. On boiling, however, it was reduced to about 1°·5. The *permanent* hardness of the water, therefore, is very low.

Mansion House, Old Park, Bristol,
May 17th, 1852.

On Hircine, a new Resin. *By* HENRY PIDDINGTON, *Curator of the Museum of Œconomic Geology, Bengal.*

I have not ventured yet to announce this as a new *mineral* resin, though I think it may be so. It was placed in my hands by Mr. Theobald, senior, with a request that I would examine it. Mr. Theobald has not yet been at liberty to furnish me with any memoranda regarding its locality, but expects soon to be able to do so.

It should be observed, that we had only a small lump of it weigh-

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ing barely an ounce troy; and it was of course desirable to keep as much of this as possible for a museum specimen.

This resin is brown on the external parts, and of a very brown-yellow colour internally. It is generally opake, but is slightly translucent at the edges. It is tough to break, and very tough and elastic, leaping out of the mortar if not covered up while pounding. Its fracture is hackly in small pieces, but conchoidal in the large. Its specific gravity is 1·10; but if freed from the external rough coat, which could not be completely divested of air-bubbles, it would probably be 1·2, or thereabouts.

It melts in the flame of a candle, and an impression may be taken upon it, resembling in this respect very bad bazaar sealing-wax.

It burns in the forceps, or in a porcelain capsule, with a blazing yellowish flame, with numerous strong jets of gas, and a dark smoke like the best bituminous coal. Towards the end of this first combustion, it swells into a round, tough, carbonaceous ball, and the flame expires. This ball has a very peculiar semi-animal odour, which may be described as that of coarse hair, or hircine, whence its name; but it is not so strong as to be altogether disagreeable. When this coal is again heated upon a large piece of platinum foil, it swells, and flames, and jets exceedingly, the gaseous emanations covering the whole of the platinum foil with flame, as if alcohol, æther, or naphtha was projected from the burning mass! When the flame expires, it leaves a very light charcoal and a coat of gray dust on the platinum. The whole of this dust and coal, when burned to a gray ash in a platinum crucible, is found by acids and the blowpipe to consist of minute portions of iron and silica without any trace of lime or alumina.

By boiling in distilled water, it softens, and the powder gives out with the steam the peculiar odour above alluded to. It does not colour the water in any material degree, but nitrate of silver renders the solution slightly turbid. When it is evaporated, a slight portion of a white gummy matter is left in the capsule, which has no smell or taste, so far at least as a minute trial with a small quantity of the resin could ascertain.

It is but little soluble in cold alcohol. In boiling alcohol about one-half of it, or less, is dissolved when powdered, giving a gold-yellow solution; the insoluble part is a brown granular residuum, and the alcohol has flaky white masses suspended in it, which do not settle. These collected on a filter give a grayish-white crust, which boiled in fresh alcohol dissolves also, leaving only a little granular deposit, the alcohol remaining colourless. Upon platinum this white crust ignites quickly with a bright white flame, and burns without any residuum, but always with the peculiar hircine odour, though not in so strong a degree. When the alcoholic solution of the white crust is evaporated, it leaves a dirty grayish-white mass, which has an agreeable odour, but does not, in the small quantity experimented upon, resemble a resin, as it coagulates in clots and masses in the watch-glass.

The alcoholic residuum is a light brown resin, which burns with

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a bright clear flame, and leaves a white powdery ash as before. The latter portions of the smoke have a musky odour, which, like the hircine one of the original resin, is not disagreeable.

This alcoholic residuum is insoluble in æther, or but very partially soluble, giving only a faint yellow colour to it.

When the pure and filtered yellow alcoholic solution is allowed to evaporate, it gives an orange-coloured resin, which burns with a bright, clear yellow flame after fusing to a bright orange-red mass.

This resin is almost totally soluble in æther, giving a bright yellow solution with but a trifling residuum. Its smell is a strong sugary one, like a cask of raisins.

In concentrated nitric acid it becomes a tough, bright, yellow, pasty and frothy mass, and partly dissolves, colouring the acid of a bright straw-yellow colour. The pasty residuum adheres somewhat to the fingers, but could not be further examined.

The nitric acid solution gives a white precipitate with carbonate of potash, which is mostly soluble in an excess of the alkali; but a portion of it remains as a silky precipitate.

In acetic acid it also gives a straw-yellow solution, which is precipitated by carbonate of potash; but this precipitate does not appear to be soluble in excess of the alkali, and is silky, like the residual precipitate from the nitric acid solution above described. When the acetic acid solution is evaporated, it gives a brown resinous-looking material, which is soluble in alcohol.

Its reactions with strong sulphuric acid are the most remarkable, and with the effect of nitric acid on the alcoholic solution seem quite to distinguish it from any of the resins or gum-resins of which we have any record*.

It dissolves almost totally (leaving only, I think, a few of the surface impurities), giving a deep blood-red solution, which appears like inspissated venous blood, which after some days changes to a deep brown. When diluted, this solution becomes of a dull, dirty, troubled white colour.

With carbonate of potash, a white, cloudy, and silky precipitate is shown.

Dropped into ammonia with precaution, it colours the solution brown; and finally, when left to settle after saturation, gives clots of a dark brown glutinous matter, which seem to be the original resin in a softened state.

It appeared worth while to examine the action of the acids on the alcoholic solution, as these effects are well marked with guaiacum and some other of the resins. The results were:—

The alcoholic solution with nitric acid diluted with one-fourth

* Mr. Hatchett, Phil. Trans. for 1806, p. 92, says, that guaiacum gives also a deep red colour to sulphuric acid, but then it undergoes various changes of colour, from green to blue and brown, when nitric acid is added to the alcoholic solution, which, as will be subsequently seen, hircine does not. Hircine in the mass looks much more like a piece of guaiacum *wood* (*Lignum vitæ*) as to colour, but not weight, than like the gum-resin of that name, which indeed it does not at all resemble.

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water, changes only from a golden-brown to a clear gold colour, and no change occurs after forty-eight hours.

The same takes place with phosphoric acid, with a slight white deposit.

With sulphuric, muriatic, and acetic acids a white precipitate is produced, which is less plentiful with the acetic acid than with the two first. In all of them the fluid shows no alteration of colour, except as above noted from a golden-brown to a clear yellow or golden colour.

We cannot, from so small a portion, form any opinion of its œconomical uses as a varnish, or for sealing-wax, or any of the purposes to which shell-lac is supplied; nor can I spare any of it to ascertain its habits with turpentine and naphtha. We are also ignorant if it is abundant, and at what rate it can be obtained.—*Journal of the Asiatic Society of Bengal*, No. 1, 1852.

ANALYTICAL CHEMISTRY.

On the Determination of Phosphoric Acid by Molybdate of Ammonia. *By* W. J. Craw, *Assistant in the Yale Analytical Laboratory.*

The determination of phosphoric acid has always been one of the most important and most difficult problems of analytical chemistry. It is very widely diffused in nature, occurring in the soil, the ashes of plants, and a great number of minerals. The bases with which it is most frequently united are iron, alumina, the alkalies and alkaline earths. Several of these combinations are decomposed with very great difficulty, the phosphate of alumina in particular resisting nearly every effort to reduce it to its component parts.

Although good methods have been proposed for the analysis of many of the simple phosphates, that of phosphate of lime for instance, yet it usually happens that several of these occur together; and until very recently no process has been devised which could effect the separation of phosphoric acid from all the bases previously mentioned, when in company.

A great amount of labour has been spent by chemists, within the last few years, in the effort to overcome this difficulty. Numerous ways have been tried with greater or less success, but most of these contain inherent difficulties, which in many cases prevent their application. Even Rose's process by carbonate of baryta, though a standing monument of profound knowledge and admirable research, is yet too complicated to yield good results, except in the hands of those who have practised it so often as to be perfectly familiar with all the necessary precautions.

The great desideratum of a simple and accurate method for the determination of phosphoric acid, with whatever substances it may be combined, has been supplied by Sonnenschein*. He states that

* Journ. für Prakt. Chem., vol. liii. p. 339.

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the yellow precipitate produced by molybdate of ammonia in the solution of a phosphate contains phosphoric acid as an essential constituent, and not, as asserted by Svanberg and Struve, an accidental admixture. From several analyses of this compound he finds it to contain about 3 per cent. of phosphoric acid. A number of trials were also made to ascertain whether by this means phosphoric acid could be separated and determined quantitatively, which were completely successful. For this purpose a large quantity of the molybdate solution is prepared as follows:—1 part of molybdic acid is dissolved in 8 parts of ammonia and 20 of nitric acid. The phosphate is dissolved in nitric acid, and there is added to it a quantity of molybdic acid equal to about 30 times that of the phosphoric acid. The solution with the precipitate is digested for some hours with the aid of a very gentle heat, filtered, and washed with the same solution which was used for the precipitation. The whole is then dissolved in ammonia, and the phosphoric acid thrown down by a magnesian salt. The presence of molybdic acid is not injurious, as the double molybdate of ammonia and magnesia is easily soluble.

Sonnenschein's experiments on the separation of phosphoric acid from alumina and other bases all gave very good results.

With the view of confirming this discovery, and also of ascertaining with more precision the cause of the peculiar behaviour exhibited by this substance towards reagents, I have made a number of trials with it. Among other substances, the action of the mineral acids and of the ammoniacal salts has been more particularly tested.

The yellow powder is found to be in—

Chloride of ammonium	easily soluble
Oxalate of ammonia	easily soluble
Sulphate of ammonia	sparingly soluble
Nitrate of potash	sparingly soluble
Chloride of potassium	sparingly soluble
Sulphate of magnesia	sparingly soluble
Nitrate of ammonia	very little soluble
Sulphate of potash	soluble
Sulphate of soda	soluble
Chloride of sodium	soluble
Chloride of magnesium	soluble
Sulphuric acid, strong and dilute	soluble
Hydrochloric acid, strong and dilute	soluble
Nitric acid, strong and dilute	soluble
Hot water	soluble

In all these cases the mixture was heated to boiling. Solutions of the caustic alkalies and the alkaline carbonates and phosphates dissolve the yellow compound even in the cold. So also do chloride of ammonium and oxalate of ammonia. The mineral acids also act upon it to some extent. Cold water dissolves it with great difficulty. It appears to be decomposed to a small extent by the combined influence of air and moisture, as it turns blue when dried in the atmosphere after washing with water. Its behaviour towards solvents is changed by the presence of molybdate of ammonia, so

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that it becomes nearly insoluble in acids even on boiling. The act of solution is, probably in all cases, attended with decomposition and removal of molybdic acid, which is prevented by the presence of molybdate of ammonia.

Some quantitative experiments were also made on the separation of phosphoric acid from the bases. It may be important to remark, that when effecting the precipitation by means of molybdate of ammonia, this, as well as the nitric acid, should be in decided excess. To ascertain when this is the case, before filtering off the solution, a drop of it may be taken up with a pipette, and transferred to a test-tube containing solution of sulphuretted hydrogen, when the brown precipitate of sulphuret of molybdenum will appear.

After separating the precipitate from the solution, the latter should always be allowed to stand for some time in a warm place, to see whether any additional precipitate is formed.

Experiments.

I. Taken 0·1199 grm. of tribasic phosphate of soda, which was dissolved in nitric acid, a pure solution of lime added, and the phosphoric acid determined according to the directions already given :—

	Calculated.	Found.
Phosphoric acid.....	0·0238	0·0243

II. Taken 0·069 grm. of phosphate of soda, and mixed with solutions of iron, alumina, lime, magnesia and potash ; the phosphoric acid then determined as before :—

	Calculated.	Found.
Phosphoric acid.....	0·0137	0·0146

III. Taken 0·0463 grm. of phosphate of soda, mixed with solutions of the same substances as in the last, and the phosphoric acid determined in the same manner :—

	Calculated.	Found.
Phosphoric acid.....	0·0092	0·0095

These results confirm those of Sonnenschein, and show that the method, as regards accuracy, is all that can be desired, while, in point of simplicity, it is superior to any of the old processes.

It will prove of especial advantage in cases where, as in the analysis of soils, a small quantity of phosphoric acid is associated with a variety of other substances existing in much larger proportion.—Silliman's *Journal*, May 1852.

PATENT.

Patent granted to A. Parkes *for Improvements in the Manufacture of Copper, and in the Separation of some other Metals therefrom, and in the Production of Alloys of certain Metals.*

The improvements in the manufacture of copper, which form the first part of this invention, consist in using iron and zinc in certain stages of the processes of smelting, whereby better copper is obtained from inferior ores than has heretofore been the case.

First, with regard to iron, it may be added to the copper when

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in the state known as "white metal," or in any of the more advanced stages, provided sulphur be present; but the following plan is preferred to be adopted:—The ores are treated as usual until the product has reached the roasting-furnace, and, by being allowed to cool therein, has become "close regule." The iron (either in the state of wrought or cast iron) is now added in the proportion of 1 cwt., or thereabouts, to a charge of about 2½ tons of the regule; the furnace doors are closed, and the heat raised; and the product is tapped as "pimple copper." In this state it is removed to the refining furnace, where it is treated in the ordinary manner; or, in some cases, it is treated with metallic zinc, as hereafter described. Sometimes, after the introduction of the iron into the roasting-furnace, the metal is run out as "light regule," and the pigs stripped in the manner practised when making best selected copper; the portions which have been stripped are then introduced into the roasting-furnace, with ½ cwt. of iron to a charge of about 2½ tons of metal; and the charge is allowed to remain in the furnace until it becomes pimple copper, which is then tapped and removed to the refining furnace, as before mentioned. This second operation with the iron will only be necessary when very pure copper is required. In some cases the iron is added to the metal in the refining furnace in the proportion of 1 cwt. to each charge of from 4 to 5 tons, then the metal is well agitated to oxidize the iron; and when it has arrived at "set pitch," it is poled in the usual manner, and laded out of the furnace; or metallic zinc may be added previous to poling, as hereafter described. The patentee does not employ iron in the refining furnace with copper which has been previously treated with iron in the roasting-furnace.

With regard to zinc, the invention consists in adding it to copper when in a fused state in the refining furnace. To each charge of 5 tons of copper, whether the same has been treated with iron or smelted in the ordinary way, about 1 cwt. of metallic zinc is added (by preference, when the copper is at set pitch); and after the charge has been permitted to remain in a melted state for a couple of hours, so that the zinc may volatilize, it is poled and laded out as usual.

The patentee states that he does not confine himself to the exact proportions above given.

The improvements in separating some other metals from copper, which constitute the second part of this invention, relate to the treatment of argentiferous compounds of that metal, and will be understood from the three following processes, which are dependent upon the discovery that silver is easily volatilized when in connexion with zinc and arsenic in a fused state, and are modifications of this discovery applied to the treatment of compounds containing silver. In carrying out these improvements, a reverberatory furnace is employed, having a flue and chambers connected therewith, suitably arranged for collecting the products that pass from the furnace; and, when so collected, they may be cupelled, or otherwise treated, to obtain the silver.

1. If the argentiferous compound is in the metallic state, and

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contains 10 oz. of silver in the ton, the patentee adds to each ton of it, when melted in the reverberatory furnace, from 3 to 5 per cent. of metallic zinc, from ¼ to ½ per cent. of white arsenic, and about ½ cwt. of anthracite coal, or other carbonaceous matter; and he then closes the furnace doors, and heats the whole together for about six hours; by which time the silver will have passed over with the zinc and other volatile metals, and become condensed in the flue and chambers connected with the furnace.

2. When the prevailing state of the compound is that of a sulphuret, it is fused in the furnace; and to each ton of it is added from 6 to 10 per cent. of calamine, or other oxidized compound of zinc, together with lime, or other flux, if required, and ½ cwt. of anthracite coal; and if the compound is free from arsenic, from ¼ to ½ per cent. of white arsenic is also added. The remainder of the process is the same as the preceding one. It is preferred to add the zinc and arsenic to the sulphuret compound when in the state of "pimple metal."

3. In case the argentiferous compound consists chiefly of oxide or carbonate of copper, then to each ton is added from 10 to 15 per cent. of blende, or other sulphur compound of zinc, from ¼ to ½ per cent. of white arsenic, and about 1 cwt. of anthracite coal, together with a flux if necessary; and then the operation proceeds as in the first and second processes. The patentee prefers to add the sulphur compound of zinc and the arsenic after the compound has been fused and skimmed to remove the earthy matters.

The above are the proportions for argentiferous compounds containing about 10 oz. of silver to the ton; but if the amount of silver be greater than this, the quantity of zinc and arsenic is increased in the same relative proportion; and when the compounds contain above 50 oz. to the ton, the zinc and arsenic should be added by degrees, instead of the whole quantity at once. The patentee states, that he has directed white arsenic to be used in the above processes only because it is the most convenient compound of that metal with which he is acquainted; but other compounds, or metallic arsenic itself, may be employed, taking care to use an equivalent proportion of the metal to that in the compound above mentioned.

The last part of the invention consists in improvements in the production of alloys, by combining nickel with chromium, and subsequently adding other metals to such alloy, according to the purposes for which it is required. The patentee prefers to take oxide of chromium and oxide of nickel in equal proportions, or 2 parts of oxide of chromium and 1 part of metallic nickel, and to fuse them together in a closed crucible, well covered with a carbonaceous flux; and having obtained this alloy, he remelts it, and adds other metals thereto in various proportions, according to the nature of the alloy desired to be produced. The following proportions have been found to produce good results when white alloys have been required:—Alloy of nickel and chromium 10 parts, and tin 90 parts; or alloy of nickel and chromium 20 parts, and iron 80 parts; or alloy of nickel and chromium 20 parts, copper 60 parts, and zinc 20 parts. —Sealed Sept. 11, 1851.

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THE CHEMICAL GAZETTE.

No. CCXXXII.—June 15, 1852.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On a new Saccharine Substance contained in the Berries of the Mountain Ash. *By* J. PELOUZE.

THE berries of the mountain ash contain among other substances malic acid, bimalate of lime and glucose. The great acidity of this fruit does not admit of our supposing the existence in it of cane-sugar. The crushed berries yield a juice which soon begins to ferment, and furnishes a vinous liquid of a very acid, and by no means agreeable taste, which in some districts is used as a substitute for cider.

The experiments of Piria on the transformation of asparagine or malamide into succinate of ammonia, those of M. Dessaignes on the conversion of malic acid, or of malic acid combined with lime, into succinic acid, led me to suspect that the latter acid might be readily obtained by the action of the atmosphere upon the juice of the berries of the mountain ash. I was disappointed in my expectation; no succinic acid could be detected in some juice which had been exposed for more than a year, but I found in it a new kind of sugar, which I propose to call *sorbine*.

Preparation of Sorbine.—The berries collected towards the end of September were crushed and pressed in linen; the juice was exposed from thirteen to fourteen months in some dishes, during which time several deposits and mouldy vegetations formed in it, which were not examined. The liquid, which had spontaneously become clear, was decanted, evaporated at a gentle heat to the consistence of a thick syrup. This syrup deposited some dark brown crystals, which were completely decolorized by being twice treated with animal charcoal.

Sorbine contains no water of crystallisation; it can be fused without parting with any water. With chloride of sodium it forms a compound which appears to crystallize in cubes. Sorbine is colourless, of an intense sweet taste, so that in this respect it cannot be distinguished from cane-sugar. The crystals are quite transparent, hard, grate between the teeth like sugar-candy, of spec. grav. 1·654; at 59° F. they are rectangular octahedra, belonging to the system of the right rectangular prism. Water dissolves nearly twice its weight of this sugar; boiling alcohol takes up but very little, and again deposits it in crystals on cooling. A concentrated solution of

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this sugar resembled completely one of ordinary sugar; the saturated syrup had a density of 1·372 at 59°. Sorbine and its syrup are therefore both somewhat denser than in the case of cane-sugar. Sorbine cannot be set in fermentation by yeast at 68°–86°; dilute sulphuric acid does not alter its properties, and does not render it fermentable after being boiled with it for half an hour, nor does this treatment change its behaviour towards polarized light. Concentrated sulphuric acid immediately attacks it; the sorbine first turns reddish-yellow, and then with a gentle heat is converted into a black mass; nitric acid converts it into oxalic acid, with copious evolution of red fumes; like cane-sugar, it furnishes more than half its weight of oxalic acid. On analysis it furnished 40·00 per cent. carbon, 6·66 hydrogen, and 53·34; and its formula is either $C^{12} H^{12} O^{12}$ or $C^{12} H^{9} O^{9}$.

Sorbine and Oxide of Lead, $C^{12} H^{9} O^{9}, 4PbO$.—A solution of acetate of lead to which a little ammonia has been added, when mixed with a solution of sorbine, parts with the whole of its lead. The white precipitate, on being washed and dried, turns yellowish, but this has no influence on the results of the analysis. At 212° it diffuses a faint odour of caramel. Several analyses furnished as a mean 74·5 per cent. of organic matter, according to which its atomic weight, referred to 1 equiv. oxide of lead = 13949·5, is 477·3. The analysis of the lead precipitate furnished—

Carbon	11·20	12	12·10
Hydrogen	1·48	9	1·50

Decompositions.—When heated with alkalies, sorbine turns yellow, and diffuses the odour of caramel; water containing two-thousandths of sorbine is distinctly coloured yellow when heated with potash. When heated with lime, sorbine dissolves a considerable quantity of it; the filtered liquid deposits a flocculent precipitate, and gives off a distinct odour of caramel. Towards baryta it behaves in the same manner. Oxide of lead dissolves in a hot solution of sorbine, but at the same time the odour of burnt sugar is perceptible. When heated upon platinum foil, it behaves like ordinary sugar, melts, turns yellow, gives off the odour of caramel, and leaves a bulky cinder. Sorbine dissolves a large amount of oxide of copper; the solution, which is of a magnificent blue colour, slowly deposits a precipitate of red protoxide of copper. The tartrate of copper and potash is likewise reduced by sorbine, both in the cold and on the application of heat.

Sorbinic Acid, $C^{32} H^{18} O^{15}$.—When sorbine is kept for some time between 302° and 356°, it is converted into a dark red mass, which consists principally of the new acid. The residue is dissolved in potash or ammonia, and the solution filtered and supersaturated with an excess of dilute hydrochloric acid, when it deposits flakes of a deep red colour, which are washed and dried between 248° and 302°.

Sorbinic acid is amorphous, of so deep a red colour that it appears nearly black; insoluble in water, alcohol and weak acids; very soluble, on the contrary, in potash, soda, and ammonia, with which it

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forms solutions of a rich sepia tint; a mere trace of acid suffices to impart a perceptible colour to alkaline water. Salts of baryta, alumina, tin, gold, iron, and platinum give bulky precipitates with soluble sorbinates of a reddish-yellow colour. Sulphate of copper gives a greenish-yellow precipitate, which dissolves in an excess of ammonia and forms a dark green liquid. The salts of cobalt and nickel differ widely in their behaviour towards sorbinate of ammonia; the salts of cobalt give a brown ochreous precipitate, insoluble in an excess of ammonia, whilst the salts of nickel give a reddish-brown precipitate, which dissolves readily and entirely in ammonia to a red liquid resembling the sorbinate of ammonia.

The analyses of sorbinic acid and of the sorbinate of lead furnished—

Acid.		Lead salt.	
Carbonic acid	57·96	Oxide of lead.....	51·35
Hydrogen	5·51	Sorbinic acid.....	48·65
Oxygen	36·53		

Admitting for the acid the formula $C^{32} H^{18} O^{15}$, the salt of lead will be $3PbO, C^{32} H^{18} O^{15}$.

Optical Properties of Sorbine.—Sorbine acts upon polarized light; dissolved in water and in acids, it deviates the plane of polarization to the left. It is the first known crystallizable saccharine substance which deviates to the left; its rotatory power was found equal to 35°·97. The dispersion which sorbine impresses upon the planes of polarization of the different rays of light is nearly identical with that of quartz. M. Bertolot, who made the observations, found $\frac{23·1}{30}$; in quartz it amounts to $\frac{23}{30}$. The rotatory power of sorbine appears to alter with the temperature of the solution, but only very little. At

41° the tint of passage occurred at −26°·19 deviation.
63° the tint of passage occurred at −27°·17 deviation.

Sorbine, which had been treated for a quarter of an hour with hydrochloric acid between 140°–158°, had not perceptibly altered its rotatory power. The number of new sugars is being rapidly increased, and it will be requisite to use great precaution in discriminating between the various species of this class of bodies. Thus it will be seen that this sugar cannot be discovered by the fermentation test, and that glucose cannot be determined by means of the tartrate of copper and potash in liquids which contain sorbine. Sorbine is interesting from its composition, the beauty and regularity of its crystals, its action upon polarized light, and its great analogy with the sugars properly so called, from which however it differs in this respect, that it does not experience vinous fermentation. Glucose at 212° and lactine at the ordinary temperature have the same centesimal composition as sorbine; their widely different properties however do not admit of their being confounded with each other.—*Comptes Rendus*, March 15, 1852.

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On the Preparation of pure Methylic Alcohol. *By* Prof. Wöhler.

The difficulty of preparing pure methylic alcohol from crude wood-spirit is well known. The following method, which is based on the property which the oxalate of methylic æther possesses of crystallizing, appears the most advantageous, at least for the preparation of small quantities. The wood-spirit is mixed with an equal weight of concentrated sulphuric acid, taking care to avoid any heating, and the brown mixture distilled in a tubulated retort with 2 parts by weight of binoxalate of potash. It is perhaps advisable, before distilling the mass, to allow it to stand for twenty-four hours. At first a volatile combustible liquid passes over, which is followed by the oxalic æther, which solidifies in the neck of the retort. The recipient is changed, and the distillation continued as long as the æther, which is driven out of the neck of the retort by a gentle heat, passes over; it is strongly pressed between blotting-paper, and freed from a small quantity of adherent volatile products over sulphuric acid, or by being kept for some time in a melted state. It is thus obtained perfectly colourless. The combustible liquid which first passed over contains a considerable quantity of the oxalic æther in solution, which may be crystallized from it by evaporation at a gentle heat. The crude wood-spirit which I used was so impure that it was rendered turbid by water; it yielded in this manner more than its weight of pure oxalic æther.

To prepare methylic alcohol from the oxalic æther, it will be advisable to distil it merely with water; thereby it is resolved into oxalic acid and methylic alcohol. On distillation with the dry hydrate of lime, it is not decomposed, and only partially on distillation with a concentrated solution of caustic potash, a very insoluble salt of potash and methyle being formed.—Liebig's *Annalen*, March 1852.

On the Action of the Hydrosulphate of Ammonia upon Nitrocinnamic Acid. *By* M. Chiozza.

M. Kopp has stated, in his investigations on the balsam of Tolu and its derivatives*, that in the reduction of nitrocinnamic acid by the hydrosulphate of ammonia, an alkaloid crystallizing in mammillated masses and a yellowish resin are formed. Having undertaken, in the laboratory of M. Gerhardt, some experiments on the nitrated derivatives of the cinnamic series, principally with the view of repeating upon nitrocinnamide the beautiful investigation of M. Chancel upon nitrobenzamide, I was first led to examine the action of the hydrosulphate of ammonia upon nitrocinnamic acid, and have arrived at results which differ from those of M. Kopp. I have not the least intention of denying the accuracy of that chemist's investigation; he operated on an alcoholic solution of nitrocinnamic acid; and it is well known that the action of sulphuretted hydrogen and of the hydrosulphate of ammonia differs frequently very much when alcoholic solutions of the nitrated substances are employed instead of aqueous solutions.

* Chem. Gaz. vol. v. p. 326.

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When nitrocinnamic acid is dissolved in hydrosulphate of ammonia, and the liquid heated to ebullition, a copious deposit of sulphur forms in the course of a few minutes. The reduction is complete if a sufficient quantity of hydrosulphate is used. On supersaturating the product with a slight excess of hydrochloric acid, a liquid is obtained, which is strongly coloured by a resin which is held dissolved in the excess of hydrochloric acid. This liquid, on filtration and evaporation at a gentle heat, furnishes after some time minute brown crystals, which are contaminated by a large amount of resin. Purified by repeated crystallization from boiling water, this new substance separates in the form of perfectly white silky needles. It yielded on analysis, after having been dried at 212°—

Carbon	74·6	74·6	9 =	74·5
Hydrogen	5·0	5·1	7	4·9
Nitrogen	10·0	..	1	9·9
Oxygen	..	..	1	10·7

Nitrocinnamic acid being $C^9 H^7 NO^4$, the new substance, which may be called *carbostyrile*, would be formed by the simple deoxidation of the nitrated acid. It is, however, probable that the action is more complex, and that there is first formed an acid, $C^9 H^9 NO^3$, which, parting with 1 atom of water, furnishes the carbostyrile.

This substance does not possess the characters of an acid or those of a base. It is tolerably soluble in boiling water, from which it separates almost entirely upon cooling. It dissolves readily in alcohol and æther, is somewhat more soluble in hydrochloric acid than in pure water, and is obtained from a boiling hydrochloric acid solution on cooling in silky needles radiating from a common centre and containing no hydrochloric acid. It is insoluble in ammonia, but it dissolves readily and without decomposition in a concentrated solution of caustic potash. It is not altered by being heated for some time with ordinary sulphuric acid, and ammonia precipitates it from the solution in a crystalline state.

When boiled with oxide of silver, it furnishes a compound insoluble in boiling water, and is again separated by acids with its properties unaltered.

When carbostyrile is submitted to the action of heat, it melts to a colourless oil, which solidifies on cooling into a mass of radiated crystals. On continuing the heat, it sublimes without decomposition in brilliant needles. When heated with some pieces of potash in a tube closed at one end, it does not give off any ammonia, but some oily drops condense in the cold portion of the tube.

This new product appears to be a volatile alkaloid similar to aniline, which it resembles by its odour. From the above reactions, carbostyrile may be regarded as the nitrite of an acid resembling carbanilic acid, in which the aniline is replaced by styriline, *i. e.* by the alkali, which ought to be obtained by the reduction of nitrated cinnamine (nitrostyrole). According to this view, carbostyrile would correspond to carbanile:—

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$C^7 H^7 NO^2$ (carbanilic acid) $-H^2 O = C^7 H^5 NO$ (carbanile).
$C^9 H^9 NO^2$ $-H^2 O = C^9 H^7 NO$ (carbostyrile).

I expect that a further examination of the alkaloid which is produced by the action of potash upon carbostyrile will justify the above opinion as to the nature of this substance.—*Comptes Rendus*, April 19, 1852.

Estimation of the Quantities of Free Acids in the Juices of Fruit. *By* M. GRÆGER.

The juices under examination are mixed with neutral tartrate of potash, and the amount of free acids calculated from the quantity of bitartrate of potash which separates. To determine the amount of free tartaric acid in a juice, a second portion is divided into two equal parts; the one is neutralized with potash, and the other half of the juice now added, and the amount of acid calculated from the quantity of precipitated bitartrate of potash.—*Jahrb. für Prakt. Pharm.*, xxiii. p. 293.

On some Constituents of Saffron (Crocus sativus). *By* M. QUADRAT.

The author prepared the colouring matter of saffron in the following manner:—The saffron was completely exhausted with æther, and then extracted with boiling water; the clear aqueous solution was precipitated with basic acetate of lead, the red precipitate which forms washed with water, suspended in water, and decomposed by sulphuretted hydrogen, and the precipitate well washed. The colouring matter was then extracted from the precipitate with boiling alcohol, the alcoholic solution evaporated to dryness in the water-bath, the residue treated with water, and the aqueous solution evaporated to dryness. The colouring substance thus obtained forms an aurora-red inodorous powder, which dissolves in water with a yellow colour; the presence of a trace of alkali increases its solubility in a high degree. It dissolves readily in alcohol, but sparingly in æther. It is decomposed by strong mineral acids; from an aqueous or alkaline solution it is separated by dilute mineral acids in brownish-red flakes, but in an altered state; the organic acids, as tartaric, tannic and gallic acids, likewise cause the separation of red flakes. Dilute solutions of the alkalies readily dissolve the pigment, and acquire a yellow colour. Concentrated solutions, at the temperature of boiling water, decompose the pigment; and on distillation, an oily substance passes over, which has a different odour from oil of saffron, is lighter than water, but after some time sinks to the bottom as a brownish mass. On heating the pure colouring substance to 248° F., it turns blackish-brown; at 302°, it becomes shining red; at 356°, red-brown, with tumescence; and above 392°, it is entirely decomposed.

This colouring matter contains no nitrogen. Dried at 212°, it furnished on analysis results leading to the formula $C^{20} H^{13} O^{11}$, viz.

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	Found.	Calculated.
Carbon	54·54	54·30
Hydrogen	5·96	5·88
Oxygen	39·50	39·82

A red compound with oxide of lead, formed by precipitating the aqueous solution with basic acetate of lead, furnished, when dried at 212°,—

Carbon	21·81	20 =	21·55
Hydrogen	2·31	13	2·33
Oxygen	15·92	11	15·80
Oxide of lead	59·96	3	60·32

The aqueous solution of the colouring matter gives with salts of copper a green, with lime or barytic water a yellow precipitate.

Saffron likewise contains a volatile oil, to which it owes its peculiar odour. On distillation with water, a yellow oil passes over, which is specifically lighter than water, has an agreeable smell, but after a short time forms a whitish mass, which sinks to the bottom.

On evaporating an ætherial extract of saffron, a yellowish fatty substance is left behind, which on treatment with hot water yields on cooling a snow-white mass, the melting-point of which is situated at about 118°. It dissolves in boiling alcohol, from which it crystallizes in part on cooling.

Saffron also contains grape-sugar and an apparently new acid. On being burnt, it furnished 8·93 per cent. of an alkaline ash, which contained carbonic acid, sulphuric acid, silica, phosphoric acid, chlorides, lime, magnesia, potash and soda.—Liebig's *Annalen*, lxxx. p. 340.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Influence of Sulphur upon the nature of Cast Irons. By M. Janoyer, *Director of the Blast-Furnaces of Orme.*

In the present memoir I shall describe some experiments which I have made in order to ascertain the influence which sulphur exercises upon the nature of cast irons. All works on metallurgy, which have treated of the action of the simple non-metallic bodies upon cast iron, point out, it is true, the tendency of sulphurous ores to produce white metal in their treatment in the blast-furnace, but not one gives any information respecting the mode of action of the sulphur. It is generally admitted that sulphur renders cast iron too fusible, and consequently difficult to convert into gray metal. This explanation, which has some truth in it, is not sufficient, seeing that very gray cast iron may be easily produced with highly phosphorized, and consequently very fusible ores. The disintegrated oolitic ores of Villebois and of Tremblois, which contain a large proportion of phosphorus, furnish tolerably good results. It is necessary

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to admit, independently of the great fusibility, some chemical action of the sulphur,—a decarbonizing action upon the iron.

The charge for the blast-furnaces of Orme, situated in the coal basin of the Loire, consists essentially of two kinds of ores, viz.

Compact peroxidized ore of Privas.		Carbonated ore of the Coal-measures.	
Clay	16·55	Clay	75·15
Peroxide of iron	70·05	Protoxide of iron	37·02
Lime	5·88	Sulphuret of iron	5·98
Water and volatile substances	7·52	Lime	0·86
		Magnesia	0·55
		Water and volatile matters	42·00
	100·00		

The first is a compact ore, of an average degree of reducibility, and tolerably fusible; the second is both easily reducible and fusible, but it contains much sulphur; the gangue of both is argillaceous.

Of these two ores, that of the coal measures (especially when calcined) presents, excepting the sulphur, all the conditions essential for gray cast iron with large and open grain; and to protect it from the great fusibility of the sulphurous cast irons, and preserve it from the action of the sulphur and silicon, which weaken the tenacity, I treated this ore with a large proportion of lime, in order to facilitate the formation of a sulphuret of calcium and a silicate of lime, and thus to get rid of these two injurious substances.

The first day, the blast-furnace working hot and very regularly, gave a very gray iron; but the nature of the product soon changed; the iron became porous (*truitée*), fibrous, white, and lastly cavernous, granular and white, although the working of the blast-furnace remained good and regular.

I had not to fear an incomplete reduction, owing to the great fusibility of the sulphuretted irons (fusion before reduction), for the corresponding slag was white, stony, and without a trace of protoxide of iron. There was no variation in the atmosphere; the blast applied preserved the same temperature and pressure; there was no alteration in the combustible, nothing, in fact, which would account for such a change in the product. I then attributed the change observed to a cooling of the lower part of the furnace, owing to the formation of the excessively basic slags which I sought to produce. Their analysis gave—

Silica	34·50	
Alumina	18·00	(without a trace of iron)
Lime and magnesia	47·00	
Sulphur	0·13	
	99·63	

To obtain a less basic slag less difficult to fuse, I progressively diminished the amount of lime. The working of the furnace continued constantly hot and regular; but the iron, instead of improving, became more and more cold. On being run from the furnace, a loud decrepitation was audible, and it quickly solidified; on fracture, it was coarse and sometimes cavernous; it exhibited in

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every respect the character of a cast iron produced with a cold working, the carburation being imperfect, although the appearances of the working, of the slag, the flame at the throat of the furnace, indicated the contrary. By diminishing the amount of flux without varying the other elements of the slag, I restored to the crucible the heat which might have been abstracted by the formation of too basic a slag; on the other hand, I isolated a larger amount of sulphur; the product became worse and worse, so that I was led to attribute to the sulphur alone the deterioration of the cast iron. I imagined that the whitening of the iron was due to the subtraction of a part of the carbon of the cast iron in the form of sulphuret of carbon, and to the heat rendered latent by the volatilization of this body. I then made various synthetical experiments, in order to prove this kind of action of the sulphur upon the carbon of the cast irons.

5 grms. of a beautiful large-grained gray iron were treated with *aqua regia*, and the solution mixed with chloride of barium; I obtained 0·02 sulphate of baryta = 0·0027 gr. sulphur, or 0·09 per cent. of the weight of the cast iron.

Knowing exactly the amount of sulphur, I resmelted—

1. 32 grms. of this same metal with 0·64 of pyrites (bisulphuret of iron), perfectly crystalline and without gangue.

2. 40 grms. with 0·40 pyrites, to see whether this iron, after whitening, would contain more sulphur, and how much it would increase or diminish in proportion as the amount of pyrites was increased or diminished. When the material was fused and very liquid, I uncovered the crucible, and perceived some brilliant globules of a more intense white than the fused metal, which were disengaged between the sides of the crucible and the metallic button, and disappeared on contact with the air, producing at this spot a very perceptible lowering of the temperature. When the disengagement had ceased, I let the metal cool very slowly in the crucible in which it had been fused, to be certain that the whitening did not proceed from a too sudden cooling. Notwithstanding this precaution, the metal, which till then had remained tranquil with a smooth surface, opened in all directions, produced a loud decrepitation, and became covered with an uneven crust, which separated partly from the metal, and presented in every respect the characters of a granular iron produced by an imperfect carburation in a bad working. When broken, the cast irons were white, and the more so in proportion to the amount of pyrites. They were excessively hard; a file of cast steel would not act upon them.

I examined these two white metals. 3 grms. of each were treated with *aqua regia*, and the solution mixed with chloride of barium. The first gave 0·19 grm. sulphate of baryta = 0·026 of sulphur = 0·87 per cent. of the weight of the metal. The second gave 0·10 sulphate of baryta = 0·0133 of sulphur = 0·46 per cent.

From these two assays it will be seen that the cast iron contains, after this fusion, a greater proportion of sulphur, and that this proportion increases almost in the same relation as that of the pyrites

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added, since in the first case we find nearly twice as much sulphur as that given in the second experiment, which contained exactly half the amount of pyrites. This is what I expected in some measure, for the pyrites loses by heat the half of its sulphur on being changed into more stable protosulphuret, and the affinity of the sulphur for the iron would necessarily give rise to the combination of the sulphur set free with the metal. The composition of the pyrites is—

Sulphur	54·26
Iron	45·74

An assay in the dry way, made with the mixture of 2 per cent. pyrites, contained before fusion 1·06 per cent. of sulphur; if the half, which was disengaged from the bisulphuret by heat, had combined entirely with the metal, I ought to have found the same amount of sulphur, whilst analysis only gave 0·87 per cent., from which must still be deducted 0·09 per cent. which the first cast iron contained, leaving 0·78 per cent. as the entire amount of sulphur which the metal took up in the fusion with pyrites. There was therefore a loss in this operation of 0·28 per cent. of sulphur.

The experiment made with the mixture of 1 per cent. pyrites, which therefore contained before fusion 0·53 per cent. of sulphur, furnished only 0·46 per cent. of sulphur, from which must be subtracted, as in the first case, 0·09 per cent. contained in the metal, leaving 0·37 per cent. In this smelting there was therefore a loss of 0·16 per cent. of sulphur.

From the results of these two experiments, it is evident,—1st, that the irons contain the more sulphur the larger the amount of pyrites present when they are resmelted; 2nd, that there is a loss of sulphur after complete fusion, and that this loss at a certain time is greater the larger the proportion of pyrites.

These facts once established, it is highly probable, if not certain, that this portion of the sulphur is lost by forming with the carbon of the irons volatile sulphuret of carbon, which produced the brilliant globules observed in the above experiments.

To arrive at a certain proof, I repeated comparatively the experiments previously made by M. Berthier upon a mixture of perfectly clean soft iron filings and pyrites. M. Berthier found, that, by fusing clean soft iron with pyrites atom for atom, protosulphuret of iron is always formed without any *loss of sulphur*. If this were the case, it is proved that the sulphur lost in the preceding experiments combined with the carbon of the irons, forming sulphuret of carbon, which had a decarburating action, and produced at the same time some latent caloric by its volatilization; for it is known that on evaporation this liquid produces a decrease of temperature capable of freezing mercury.

I made a first experiment by fusing in a naked crucible before the forge 20 grms. of soft iron filings, well-cleansed, with 0·40, *i. e.* 2 per cent. of pyrites. To avoid a slight oxidation by the air which might have entered the crucible, I covered it with a piece of

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coke; and when the whole mass had arrived at a white welding heat, I uncovered the crucible to see whether in this case there was any liberation of brilliant globules, as in the fusion of the iron with 3 per cent. of pyrites; I could perceive none, the mass remained quiet, and when cold presented the form of a tolerably-compact, uniform button; on being broken, some rather dark yellowish-brown sulphuret of iron was apparent here and there, which was without a doubt protosulphuret disseminated throughout the mass. This first experiment I considered a proof of the formation of sulphuret of carbon by the fusion of gray iron in the presence of pyrites, as only in this case did I observe the liberation of brilliant globules.

I made a second experiment, in which I determined the amount of sulphur. 2·31 filings of well-cleansed iron wire were fused with 2 per cent. of pyrites; I obtained a well-fused compact button, which was easily acted upon by the file. 1·05 was treated with nitro-muriatic acid; it dissolved slowly, but entirely; the solution was precipitated by chloride of barium, and I obtained 0·08 grm. sulphate of baryta, or =1·04 per cent. of sulphur, instead of 1·05 per cent., which the mixture must have contained before the fusion. I thence concluded, as M. Berthier had done, that in the fusion of clean soft iron with pyrites, there is never any loss of sulphur. Therefore, as I have stated at the commencement, we must not attribute to the too great fusibility alone the tendency which sulphurous ores have to yield white irons. The principal cause is due to the formation of a sulphuret of carbon, which acts by decarbonizing in part the metal, and by producing a considerable lowering of the temperature from the caloric rendered latent by the volatilization of this product.

I have stated above, that, on fusing gray metal with variable proportions of pyrites, it became deteriorated, and I have supported this statement by experiments. It remained to be seen whether the same would occur, if, instead of operating upon the cast iron, we were to take the ores. I therefore reduced 20 grms. of the Privas ore with 2 grms. of lime, the whole mixed with 2 per cent. of pyrites in a crucible lined with charcoal. The metal was allowed to cool very slowly in the crucible; but notwithstanding this precaution, the fracture of the button was entirely white, and exhibited in the portion in contact with the slag some yellow plates of sulphuret of iron. Throughout its thickness it presented large cavities coated with filamentary crystallizations of sulphuret of iron. In the massive portions, the metal had a granular appearance. Altogether it was very bad, exceedingly brittle, and exhibited not the least elasticity under the hammer.

20 grms. of the same piece of ore, reduced in a lined crucible with 2 grms. of lime and 1 per cent. of pyrites, likewise furnished a very white metal, although cooled very slowly. The button exhibited, like the preceding one, large cavities coated with filamentary crystallizations; the iron was bad and brittle, and without elasticity. The only difference was, that there were no yellow plates of sul-

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phuret of iron perceptible at the junction of the metal and of the slag.

To be certain that, on treatment in the blast-furnace, the pyrites, or rather the sulphur of the pyrites, was an obstacle to the production of a gray metal, I treated 20 grms. of the same piece of ore which had served for the preceding experiments with the same amount of flux without any addition of pyrites. The metal obtained was gray, without however being graphitous; it yielded slightly to the hammer, was perfectly compact in the interior, and showed no sulphurous crystallizations. I was however able to distinguish with the aid of the lens some minute filaments of sulphuret of iron at the place of contact of the slag with the metal. On analysis, I obtained but a trace of sulphate of baryta.

I now proceeded to determine the amount of sulphur in the metal obtained in the two first experiments, by reducing the ore in the presence of pyrites, in order to see whether also in this case, acting upon the ores and not on the metal, the latter would contain an amount of sulphur greater in proportion to the quantity of pyrites present. The experiment which had been made with the mixture of 2 per cent. of pyrites furnished, on the analysis of 1 grm., 0·07 sulphate of baryta=0·96 per cent. of sulphur. As the mixture contained previous to fusion 1·06 per cent., we have a loss of 0·10 per cent.

1 grm. of the metal obtained in the experiment made with 1 per cent. of pyrites furnished 0·03 grm. sulphate of baryta =0·41 per cent. of sulphur; since the mixture contained 0·63 per cent. of sulphur, we here again meet with a loss of 0·12 per cent.

It is evident, from these experiments, that the metals contain the more sulphur the more the ores from which they are produced contained pyrites, the proportion of flux remaining invariable.

In order to prevent the injurious influence of the sulphur upon the iron in the treatment of pyritous ores in the blast-furnace, I increased progressively the amount of flux; for, according to M. Berthier, the lime decomposes a considerable quantity of sulphuret of iron at a high temperature in the presence of carbon. In order not to interfere with the fusibility of the slag, I first of all endeavoured to ascertain the maximum quantity of lime it might contain. By fusing together the clay and the lime, experiment led me to the following composition as the limit which should not be exceeded:—

Silica	36·00
Alumina	10·00
Lime	54·00

Having made this experiment, I obtained, by adding gradually lime to the charge of the blast-furnace, a white stony slag containing not a trace of oxide of iron, and approaching closely to the above composition; there were here and there particles of uncombined lime mechanically intermixed. The working of the blast-furnace was constantly good and regular, the combustible very good, and the blast heated to 750° so as to restore the heat abstracted by this enormous amount of lime.

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Notwithstanding this maximum amount of flux added to the charge, I was not able to prevent the action of the sulphur; and to obtain good *gray* metal, it was necessary to subtract a large quantity of the highly pyritous ores of the coal measures.

I next proceeded to ascertain what became of the sulphur on effecting the reduction in lined crucibles. I took,—I. 10 grms. of the ore from Privas, 5 grms. of the slag from the blast-furnace, 5 grms. of lime and 0·20 of iron pyrites; II. 10 grms. of the ore from Privas, 5 grms. of slag, 10 grms. of lime and 0·20 of iron pyrites.

The two experiments succeeded perfectly. The first gave a well-fused, vitreous, bright gray slag. However, throughout the portion of the slag which surrounded the button, a hard, whitish-yellow, compact substance, with a smooth fracture, was disseminated. The button of metal was quite white, with a very irregular fracture, very cavernous, and exhibiting a few filaments of a sulphurous crystallization. Three little balls of metal, which did not adhere to the button, but rested above the slag, had escaped the decarbonizing action of the sulphur; for with a lens, and even with the naked eye, several large laminæ of graphite were perceptible, and the metal was perfectly black. The mixture of the ore, lime, and pyrites not having been perfect, a small quantity of the ore had been reduced protected from the action of the sulphur, which, on the contrary, had strongly acted upon the button of metal. On analysis, 1 grm. of this white iron gave 0·009 sulphate of baryta =0·1242 per cent. of sulphur.

The second experiment, in which there was double the amount of flux,—the maximum quantity for the fusibility of the slag,—furnished a grayish-white slag filled pretty uniformly with the yellowish-white substance, which in the previous experiment had occurred here and there disseminated in the scoria; it had a shining yellow appearance, and when exposed to moist air, fell for the greater part into a powder, and furnished an enormous quantity of quick-lime. Notwithstanding the powerful affinity which this large amount of lime must have presented for the sulphur, the metal was entirely white, with a granular cavernous appearance, but exhibited no trace of a sulphurous crystallization; it was much more malleable than that obtained in the preceding experiment; it was rather difficult to reduce to powder, and in the mortar flattened out. Although white, it was easy to observe that there was a great improvement in its tenacity. 1 grm. of this whitish metal gave 0·005 sulphate of baryta =0·069 per cent. of sulphur, which is scarcely more than half the quantity found in the preceding experiment.

From these two conclusive experiments it is seen, that the amount of sulphur in cast iron diminishes in proportion as the amount of lime contained in the slag increases, but that it is impossible, in certain cases, to remove it altogether without rendering the slag infusible. I have stated, in speaking of the experiment made by fusing 10 grms. of the Privas ore, 5 grms. of slag, 5 grms. of lime and 0·20 pyrites, that the slag which surrounded the button was altogether compact and yellowish-white, whilst the rest of the scoria was

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vitreous, and showed nothing similar. The analysis of this portion proves, from the presence of the large amount of sulphur, that some sulphuret of calcium is mixed with the slag; and from its being in immediate contact with the whitened metal, it is evident that the sulphuret of calcium has been formed by some sulphurous emanations from the metal. This slag had the following composition:—

Silica	40·07
Oxide of iron and alumina	15·00
Lime	43·75
Sulphur	0·50

On comparing the result obtained in the analysis which gave 0·069 per cent. of the weight of the metal with the sulphur previously found in a very gray metal (0·09 per cent.), it is quite evident that the whitening must not be attributed to the sulphur combined with the iron,—sulphur which might form a true sulphocarburet of iron and prevent the isolation of the graphite. It is owing to the loss of sulphur,—as shown by the two experiments made by fusing at first gray metal, and subsequently clean soft iron with pyrites,—which combines with the carbon, forming very volatile sulphuret of carbon and rendering a large amount of caloric latent. Hence we have the whitening produced by two simultaneous actions,—subtraction of a portion of the carbon of the cast irons, and lowering of the temperature from the volatilization of the sulphuret of carbon.

With respect to the position in which the sulphuret of carbon is formed in the blast-furnace, it may be admitted that it is produced wherever the temperature is at a red heat, bearing in mind that Lampadius detected sulphuret of carbon by heating to redness some pyrites and charcoal, and that these conditions occur in the blast-furnace. On the other hand, the analyses of the gases by M. Ebelmen have not shown its presence, although the latter assumes that probably the sulphur exists in the gases in the state of sulphuret of carbon, but in inappreciable proportion. We must therefore attribute its absence to the highly reductive properties which the sulphuret of carbon possesses, which could not exist in the presence of oxide of iron. In proportion as it was formed, it would be decomposed into sulphuret of iron and oxide of carbon.

It is also possible that the pyrites, on losing the half of its sulphur by heat, yields it to the iron already reduced, converting it into protosulphuret without the formation of any sulphuret of carbon, and we arrive at the same result, that is, the conversion of the iron into protosulphuret in its progress through the furnace.

The flux not having lost the whole of its carbonic acid, does not possess sufficient affinity for the sulphur to decompose the protosulphuret of iron which is constantly being formed. It is only in the neighbourhood of the *tuyères*, when the flux has been entirely changed into caustic lime and partially into calcium, that the affinity of the carbon in a nascent state (graphite), together with that of the lime for the sulphur, determines the decomposition of a part of the protosulphuret of iron. There is then formed sulphuret of

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carbon at the expense of the carbon of the cast iron, and caloric thereby rendered latent. Another portion of the sulphur combines with the calcium.

The sulphuret of carbon formed in the crucible itself must be again partially burnt by the blast, from which would result sulphurous and carbonic acids, which would reproduce some sulphuret of iron and calcium, and oxide of carbon; and it should be remarked here, that the proportion of sulphuret of calcium will be the more considerable the greater the amount of lime present in the charge. It follows from this, that in order to obtain a metal which shall contain the minimum amount of sulphur, it is necessary that the slags should contain the maximum amount of lime. I may also add, that in this case the working of the furnace should be as hot as possible, in order to facilitate the isolation of the graphite, and consequently the formation of the sulphuret of carbon, which serves to transfer the sulphur from the metal to the slag.

The author observes, in conclusion, that a considerable improvement has recently been effected in the working of the blast-furnaces and their products by washing the coals, which removes a great portion of the pyrites, and also, by getting rid of the earthy matters, increases the heating power of the coal.—*Annalen des Mines*, Feb. 1852.

On Dyeing with Sandal-Wood. *By* Anton Wimmer.

In order to dye as fine a red with sandal-wood as with madder, the author first exhausts the wood with boiling water. He then treats it with a cold filtered solution of chloride of lime as long as this becomes coloured, and washes it perfectly with pure water. From the sandal-wood thus prepared the red colouring matter is extracted by a hot, but not boiling solution of soda, the wood being tied up in a linen bag; the kettle is to be covered with a well-fitting lid. The extract should have a deep red colour tending to violet. Cotton, linen, and woollen stuffs are prepared with acid mordants, and dyed in it in the usual manner. The author obtained a beautiful scarlet by alternately treating the stuffs with a mordant of chloride of zinc and the above bath. The colours are durable, and particularly useful in saving cochineal, as stuffs which are to be dyed with cochineal may previously receive a ground of the colouring matter of sandal-wood.—*Kunst und Gewerbebl. für Baiern*, 1852, p. 149.

Process for giving various Objects a Pearly Lustre. *By* O. Reinsch.

To produce the iridescence of mother-of-pearl on stone, glass, metal, resin, paper, silk, leather, &c., Reinsch adopts the following process:—2 parts of solution of copal, 2 parts of that of sandarach, and 4 parts of solution of Damara resin (equal parts of resin and absolute alcohol) are mixed with half their volume of oil of berga-

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mot or rosemary. This mixture is to be evaporated to the thickness of castor oil. If this varnish be then drawn by means of a feather or brush over the surface of some water, it will form a beautifully iridescent pellicle. This film is now to be applied to the objects which are to be rendered iridescent. The vessel in which the water is contained, on which the pellicle has been produced, must therefore be as large as, or larger than, these objects. The water should have about 5 per cent. of pure solution of lime added to it; its temperature should be kept at about 72°. The objects are dried in the air.—*Kunst und Gewerbebl. für Baiern*, 1852, p. 165.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

April 19th, 1852. (Professor Daubeny, President, in the Chair.) The following paper was read:—

"Researches on the Constitution of Organic Acids," by M. Charles Gerhardt.

The experiments described in this communication were instituted with the view of establishing a general formula for organic acids, which should be to them what the formula for ammonia is to the organic alkalies. The author believes that water, the molecule of which he assumes to consist of 1 atom of oxygen and 2 atoms of hydrogen, may be taken as the type of organic acids, the two atoms of hydrogen being capable of being replaced by simple metals, or by complex groups, such as methyle, æthyle, &c. Reference is made to the results obtained by Dr. Williamson and M. Chancel, tending to prove that alcohol, æther, and their homologues, represent molecules of water in which the two atoms of hydrogen are partly or wholly replaced by complex groups; in accordance with which theory the compound formed by replacing 1 atom of hydrogen in alcohol by potassium may be considered as the potassium salt of a weak acid, æthylic acid, which gives rise to a chloride (hydrochloric æther or chloride of æthyle) when acted upon by perchloride of phosphorus. Reference is also made to the experiments of Cahours, proving that various organic acids, such as benzoic, nitrobenzoic, cuminic, anisic and cinnamic acids, experience similar changes under the influence of the same reagent.

Starting from this point, the author concluded, that, by imitating the well-known reaction of æthylate of potassium on chloride of æthyle, but substituting the corresponding compounds of one of the above-mentioned acids for those of æthyle, the anhydrous acids ought to be obtained—a result which was fully confirmed by experiment. With benzoate of soda and chloride of benzoyle the experiment succeeded perfectly well when conducted in the following way:—The soda salt was well dried and mixed with an equivalent weight of the chloride, and the mixture heated to 130° Cent., when it formed a limpid liquid, which at a temperature a few degrees higher underwent decomposition, the peculiar smell of the chloride

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of benzoyle disappearing, and chloride of sodium being deposited. The product, suspended in cold water, and washed with carbonate of soda, left a white substance without odour and perfectly colourless, which was found on analysis to be *anhydrous benzoic acid*—

$$C^{14} H^{5} O^{3}.$$

This new product crystallizes in oblique prisms, which melt at 33° C. It is volatile without decomposition, insoluble in water, but soluble in alcohol and æther, and these solutions are perfectly neutral. Boiling water transforms it by degrees into common benzoic acid.

Experiments were made in the same direction with other acids, the detailed account of which the author defers for a future communication.

"Note on the Preparation of Carbonate of Amyle," by John A. Bruce.

Carbonate of amyle was prepared some years ago by Mr. Medlock, by treating fusel oil with phosphene gas, and decomposing the chlorocarbonate thus formed by heating it with water. The author adopted for its preparation the process which originally furnished the corresponding compound of the æthyle series, and which consists in heating the oxalate with potassium. When potassium comes in contact with perfectly dry oxalate of amyle, it is rapidly attacked, a brown mass is formed around the metallic globules, and a colourless inflammable gas is disengaged. On distilling the brown fluid, a mixture of carbonate of potash and charcoal is left, and a pale yellow liquid passes over, which consists of not less than four different substances, namely, carbonate of amyle, fusel oil, oxalate of amyle, and a dark viscous substance having a powerful odour. The portion distilling at 226° C. was proved by analysis to be carbonate of amyle, $C^{10} H^{11} CO^{3}$. Its specific gravity at 60° F. was 0·9065.

"New Formation of Salicylic Acid," by Dr. Gerland.

In a comparative investigation of the three isomeric acids, the benzamic acid of Zinin, the anthranilic acid of Fritzsche, and the carbanilic acid of Chancel, the immediate object of which was to test the frequently-asserted view that these acids might be identical, Dr. Gerland obtained evidence that benzamic and anthranilic acids not only differ in their chemical properties, but yield, under similar circumstances, very different, and sometimes very interesting products of decomposition. One of the most interesting of these changes occurs when anthranilic acid is treated with nitrous acid. If nitrous acid, prepared by the action of nitric acid on arsenious acid, be passed through a warm dilute solution of anthranilic acid as long as nitrogen is disengaged, the solution remains clear, and deposits on evaporation fine long needles of an acid free from nitrogen, and having the composition and properties of salicylic acid. With salts of sesquioxide of iron it yields the characteristic violet colour produced by salicylic acid under the same circumstances; and on dry distillation a considerable quantity of phenole is produced, a portion of the acid subliming unchanged.

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A dilute aqueous solution of benzamic acid also undergoes a change when exposed to the action of nitrous acid, but not a trace of salicylic acid is in this case produced.

May 3rd, 1852. (Robert Warington, Esq., Vice-President, in the Chair.) The following papers were read:—

"On the Preparation of Anhydrous Acetic Acid," by M. Charles Gerhardt.

The author states that he has succeeded in preparing anhydrous acetic acid in a state of perfect purity, and giving by analysis numbers exactly agreeing with those calculated from its formula. It is obtained by mixing perfectly dry fused acetate of potash with about half its weight of chloride of benzoyle, and applying a gentle heat, when a limpid liquid distils over, which, after being rectified, has a constant boiling-point of 279° F., is heavier than water, with which it does not mix until after it has been agitated with it for some time. It dissolves at once in hot water, forming hydrated acetic acid.

"Chemical Memoranda," by Robert Warington.

Under this head the author notices—

1st. A curious form of crystallization of iodide of potassium, in which the salt assumes the appearance of square prisms of considerable length and of varying diameter, being apparently formed by the superposition of cubes of different sizes. The measurements of some crystals of this kind are given.

2nd. A method of detecting qualitatively small quantities of oxide of copper in solution, by the addition of ferrocyanide of potassium to the solution to be tested, to which excess of ammonia has been previously added. The ferrocyanide of copper is held in solution by the ammonia, and is afterwards deposited from the filtrate as the ammonia is allowed to evaporate.

3rd. Some additional facts relating to the green teas of commerce. In a former communication the author had stated that much of the green tea of commerce was coloured with prussian blue, turmeric and gypsum. He has since found that indigo is sometimes substituted for prussian blue.

"On the Action of Ammonia upon Binoxysulphocarbonate of Amyle," by Matthew W. Johnson.

The object of this investigation was to obtain and examine the compound in the amyle series homologous with the xanthamide obtained by M. Debus by the action of ammonia on binoxysulphocarbonate of æthyle.

The process adopted consisted in adding a concentrated aqueous solution of ammonia to binoxysulphocarbonate of amyle, and digesting them together at a slightly-elevated temperature. The mixture becomes turbid, sulphur is deposited, and a yellow liquid, through which oily particles are seen suspended, floats above. When 1 part by bulk of binoxysulphocarbonate of amyle is treated with 3 parts of ammonia, a semi-solid mass results, which on being diluted with water and washed on a previously-moistened filter, is separated into solution of amyloxanthate of ammonia, which passes through,

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and a mixture of xanthamylamide and sulphur, which are retained on the filter. On putting these latter on a dry filter, xanthamylamide passes through freed from the sulphur.

The analysis of this oily product, the products of its decomposition, and the examination of the compound which it forms with chloride of mercury, establish the existence, in the amyle series, of a substance homologous with the xanthamide of the æthyle series.

Direct experiment also proved that the body formed simultaneously with the xanthamylamide was amyloxanthate of ammonia.

"On a new Process for the Detection of Fluorine when accompanied by Silica," by George Wilson, M.D., F.R.S.E.

This process is founded upon the very familiar fact, that when a fluoride, combined or mixed with silica, is heated with oil of vitriol, the fluorine and silicon are evolved in combination as the well-known fluoride of silicon; and it is applicable to all silicated fluorides which yield this gas. It is also applicable to compounds containing mere traces of fluorides, but free from silica, which are brought within the compass of the process by the deliberate addition of silica to them, so as to admit of their being heated in large quantity with oil of vitriol in glass vessels. In either case, the fluoride of silicon set free is conveyed by a bent tube from a flask or retort into water. The resulting solution, containing some gelatinous silica, is supersaturated with ammonia and evaporated to dryness, during which process the fluoride of silicon and ammonia is resolved into silica, which is rendered insoluble, and fluoride of ammonium, which is dissolved by digesting water on the evaporated residue. The solution is then evaporated to dryness, and heated with oil of vitriol in a platinum crucible covered by a piece of waxed glass.

PATENT.

Patent granted to Stephen Moulton, *for Improvements in the Preparation of Gutta-Percha and Caoutchouc.*

This invention consists in the discovery of a new combination of several materials, by which a new and valuable compound is produced.

It is a fact well known to persons acquainted with the native gutta-percha, that it is very materially affected by the change of climate; that it becomes rigid when exposed to a low degree, and soft when exposed to a high degree of temperature; that it does not at any time possess any elastic properties; and that these liabilities to change with the climate, and also its non-elastic qualities, prevent the native gutta-percha from being applied to a great variety of useful purposes. Now one part of this invention consists in obviating these disadvantages, by combining gutta-percha with a mixture of sulphite or hyposulphite of lead or zinc and the artificial sulphuret of lead or zinc, and submitting the compound to the action of a high degree of heat; whereby a material is produced which

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the patentee calls cured gutta-percha, possessing the quality of elasticity, unaffected by changes of temperature, and resisting the solvents of the native gum. The mode of making the compound is as follows:—After the gutta-percha has been cleansed from its impurities, the patentee takes 1 or more pounds weight of it, as can be conveniently ground or mixed at a time, and adds from 2 oz. to ½ a pound of the sulphite or hyposulphite of lead or zinc and the artificial sulphuret of lead or zinc, in about equal proportions of each, together with from 2 to 12 oz. of Paris white or powdered chalk; and he grinds the whole between heated rollers, and treats the mixture in the manner set forth in the specification of his patent of February 8th, 1847, for "improvements in treating caoutchouc with other materials, to produce elastic and impermeable compounds," to which specification he particularly refers for the mode of carrying out this part of the invention.

The invention further consists in combining 1 part of gutta-percha and 1 part of caoutchouc, or, as the case may require, a greater or less proportion of either the one or the other, with the sulphite or hyposulphite of lead or zinc and artificial sulphuret of lead or zinc, in about equal proportions of each. 1 lb. weight of the compound of gutta-percha and caoutchouc is combined with from 2 to 6 oz. of the before-mentioned materials, to which as a dryer from 2 to 12 oz. of powdered Paris white or chalk are added; and this compound is prepared and treated in every respect the same as gutta-percha alone. The same machinery is used, and it is exposed to the same degree of heat, producing a fabric equally as valuable for many purposes, rather more elastic, but not as capable of so perfectly resisting the action of oils as when gutta-percha alone is used.

When it is desired to produce a hard-cured gutta-percha composition, or gutta-percha and caoutchouc composition, similar to horn or ivory, from 2 to 12 oz. of calcined magnesia are added to each pound of gutta-percha compound, alone or combined with caoutchouc; and the compound is treated in all respects the same as when the magnesia is not used.

After the gutta-percha, or the gutta-percha and caoutchouc, has been ground and mixed, the compound is still liable to be affected by changes of temperature and the action of solvents, the same as in the natural state; to prevent which, the compound, whether in the form of coated cloth, sheet gum, moulded or any other article, should be placed in a room or vessel as nearly air-tight as possible, and subjected to steam or dry heat of from 250° to 350° F. The time required for thus curing the compound will vary from two to ten hours, or thereabouts, according to its thickness, and the quantity of the goods put in a mass together for this part of the process of the manufacture.

After the goods have undergone the curing as above (if properly done), they will be found not only impermeable to wet, but extremely tenacious, possessing the elastic property of the cured caoutchouc, and also unaffected by changes of temperature.—Sealed August 14th, 1851.

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THE CHEMICAL GAZETTE.

No. CCXXXIII.—July 1, 1852.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Chemical Examination of the Root of Rubia tinctorum. *By* Prof. ROCHLEDER.

ROCHLEDER not long ago described*, under the name of ruberythric acid, a substance which is remarkable from its behaviour towards acids and alkalies, by the action of which it is resolved into sugar and alizarine. The substance was dried for analysis *in vacuo* over sulphuric acid. The author has now produced acid dried at 212°, which has been analysed by R. Schwartz. Its analysis gave 54·42 per cent. of carbon. The substance, dried *in vacuo*, gave 54·54 per cent. of carbon. No more water is therefore driven off from the ruberythric acid at 212°.

The decomposition of ruberythric acid into alizarine and sugar cannot be effected by emulsine; the acid remains unchanged. This negative result of the use of the ferment from almonds is no proof that ferments may not be contained in madder or other plants, which may effect the decomposition with ease.

There is a close affinity between alizarine and chrysophanic acid. Calculated according to the atomic weights at present accepted, the composition of this acid, according to previous analyses, is as follows:—

Carbon	67·91	68·10	20	1500·0	68·18
Hydrogen	4·56	4·60	8	100·0	4·55
Oxygen	27·53	27·30	6	600·0	27·27

This colouring matter was afterwards found by Schlossberger and Döpping in rhubarb root†, and analysed with the same results. The formula $C^{20} H^8 O^6$ might be considered, as was observed at that time, as naphthaline, $C^{20} H^8$, with 6 equivs. of oxygen. Regarded as a hydrate, its formula is $C^{20} H^7 O^5 + HO$. According to this formula, chrysophanic acid is distinguished from alizarine by its containing 1 equiv. more hydrogen and 1 equiv. less oxygen, $C^{20} H^7 O^5 = C^{20} H^6 O^6 + H - O$. According to this view, there subsists the same connexion between chrysophanic acid and alizarine as between aldehyde and acetic acid.

The near relationship which is indicated by the composition ac-

* Chem. Gaz., page 21 of the present volume. † Chem. Gaz., vol. iii. p. 9.

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quires yet more probability from the great resemblance between the properties of these two bodies :—

Chrysophanic acid.	*Alizarine.*
Golden-yellow needles.	Orange-yellow needles.
At an elevated temperature, partly volatile in an undecomposed state, leaving a residue of carbon.	Partially volatile in an undecomposed state at an elevated temperature, leaving a residue of carbon.
Nearly insoluble in cold water; sparingly soluble in boiling water.	Insoluble in cold water; sparingly soluble in hot water.
Soluble in alcohol and æther, producing an intense yellow colour.	Soluble in alcohol and æther, producing a deep yellow colour.
Soluble in concentrated sulphuric acid, without decomposition, producing a blood-red colour. Precipitated in yellow flakes from the solution in sulphuric acid by the addition of water.	Soluble in concentrated sulphuric acid, producing a red colour. Precipitated unchanged in yellow flakes on the addition of water.
Soluble in solutions of potash and soda, producing a beautiful red colour. The solutions are decolorized by acids, which throw down yellow flakes.	Soluble in a solution of potash, producing a beautiful red colour by transmitted light, a violet-blue colour in reflected light. The solution is decolorized by acids, which throw down yellow flakes.
The ammoniacal solution is blood-red.	The ammoniacal solution is purple-red.
The dried compound formed with potash is indigo-blue.	The compounds formed with potash and baryta are deep violet.

The lead salt of chrysophanic acid is of a vermilion colour, like the lead salt of ruberythric acid. The alkaline solutions of chrysophanic acid are not distinguishable from those of purpurine.

The numbers which Debus procured in the analysis of purpurine and of the compounds formed by it with lead, led him to adopt the formulæ $C^{15} H^5 O^5$ and $C^{15} H^4 O^4$, PbO. Strecker and Wolff calculate the following formulæ for the same substances :—

$$C^{18} H^6 O^6 \text{ and } 5(C^{18} H^5 O^5) + 6PbO = 4(C^{18} H^5 O^5, PbO) + C^{18} H^5 O^5, 2PbO.$$

According to Strecker and Wolff, purpurine gives by oxidation the same products as alizarine, oxalic and phthalic acids. They mention that a difference of 2 equivs. of carbon between two nearly allied bodies is an unusual proportion. This anomaly disappears if we accept the formula $C^{60} H^{20} O^{20}$ for purpurine. The formula of the lead compound of Debus is therefore $= C^{60} H^{16} O^{16} + 4PbO$. 4 equivs. of water are displaced by 4 equivs. of oxide of lead.

Purpurine, according to this formula, would be distinguished

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from alizarine by an atomic weight three times as high, and by containing 2 additional equivs. of water in a free state. From this it might be explained how it yields the same products on oxidation as alizarine.

1 equiv. of purpurine would form 3 equivs of alizarine by the loss of 2 equivs. of water; and this alizarine would be changed into oxalic and phthalic acids by assimilating oxygen.

Strecker and Wolff obtained purpurine, free from alizarine, from fermented madder. It might be supposed that the formation of purpurine in this case was analogous to that of the potato fusel oil in vinous fermentation. As Liebig remarks in his Chemical Letters, 2 equivs. of potato fusel oil may be formed when 5 equivs. of alcohol give off 6 equivs. of hydrogen and oxygen in the form of water. When ruberythric acid is decomposed in the fermentation of madder, purpurine, alcohol and carbonic acid, or purpurine and lactic acid, may be formed instead of 1 equiv. of sugar and 3 equivs. of alizarine.

3 equivs. of alizarine, $=C^{60}H^{18}O^{18}$, may produce 1 equiv. of anhydrous purpurine by the elimination of 2 equivs. of hydrogen and oxygen.

The author has convinced himself, that madder kept in damp places, when it began to grow mouldy on the surface, contained much less ruberythric acid than before.

Anderson, some years since, published an examination of some colouring matters obtained from the *Morinda citrifolia**, also belonging to the *Rubiaceæ*. He found in the root of this plant, which is employed in the East Indies in dyeing, a yellow colouring matter, which he called morindine, and which could be converted by sulphuric acid and dry distillation into another colouring matter, morindone. This morindone appears to be nothing but alizarine, and his morindine merely ruberythric acid, as may be seen by a comparison of their properties. Anderson gives the formula $C^{28}H^{15}O^{15}$ for morindine, and for morindone $C^{28}H^{10}O^{10}$. According to this, morindone is formed from morindine by the loss of 5 equivs. of water.

Anderson was unable to dye stuffs, prepared with a mordant of alum or iron, with morindine; neither is it possible to dye stuffs, similarly prepared, with ruberythric acid. The only difference between morindine and ruberythric acid is, that, according to Anderson, morindine separates from a boiling watery solution in gelatinous flakes, which exhibit no traces of crystallization and obstruct the filter during filtration; whilst a hot solution of ruberythric acid, on cooling, lets fall flakes consisting of crystals.

According to the analysis which Anderson made of morindine, that substance, dried at 212°, gave 55·42 per cent. of carbon and 5·11 per cent. of hydrogen on an average of three combustions. This composition agrees with that possessed by ruberythric acid as regards the hydrogen; in carbon it differs 0·89 per cent. Anderson

* Chem. Gaz. vol. vi. p. 313.

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states that his morindine had been freed from a small quantity of lime by alcohol acidulated with muriatic acid. It might very possibly have happened that a trace of alizarine was formed, which would need to be only in very small quantity to raise the quantity of carbon 0·89 per cent.; for alizarine, dried at 212°, contains more than 14 per cent. more carbon than ruberythric acid.

The identity of morindone with alizarine is also in the highest degree probable.

The *Morinda citrifolia* appears in fact to contain the same colouring matter as the *Rubia tinctorum*. Anderson observed this similarity, but was unable to trace it out at that time, as the knowledge of the colouring matters of the madder was still extremely imperfect. Anderson, as already mentioned, has calculated the formula $C^{28}H^{15}O^{15}$ for morindine. The analyses of ruberythric acid agree equally well with the formula $C^{56}H^{31}O^{31}$ as with $C^{72}H^{40}O^{40}$, as the following calculation shows:—

Carbon	54·54	56 =	54·64
Hydrogen	5·16	31	5·04
Oxygen	40·30	31	40·32

The analysis of the ruberythrate of lead agrees equally well with the formula $C^{14}H^{7}O^{7}, 2PbO$:—

Carbon	22·74	14 =	22·70
Hydrogen	2·00	7	1·89
Oxygen	15·82	7	15·13
Oxide of lead	59·44	2	60·20

A small excess of ruberythric acid and a corresponding diminution in the quantity of oxide of lead might be explained by an incipient decomposition of the salt produced by the washing. If the quantity of oxide of lead be deducted, the composition of the substance combined with the oxide agrees exactly with the formula $C^{42}H^{22}O^{23}$:—

Carbon	56·07	42 =	56·00
Hydrogen	4·93	22	4·89
Oxygen	39·00	22	39·11

If this formula be regarded as the correct one, the rational formula of the free acid would be $C^{56}H^{31}O^{31}=(C^{14}H^{7}O^{7})+3HO$. The lead salt would be $=C^{14}H^{7}O^{7}+2PbO$; or, to be still more exact, the substance contained in the lead salt would be constituted according to the formula $C^{42}H^{22}O^{23}=3(C^{14}H^{7}O^{7})+HO$. The formation of sugar and alizarine would take place according to the equation $C^{14}H^{7}O^{7}=C^{10}H^{3}O^{3}+C^{4}H^{4}O^{4}$. The group $C^{4}H^{4}O^{4}$, by tripling the atomic weight, would give $C^{12}H^{12}O^{12}$=sugar, whilst $C^{10}H^{3}O^{3}$ represents half an equivalent of alizarine.

According to this, ruberythric acid comes into close connexion with the other matters contained in *Rubia tinctorum*. The rubichloric acid, which occurs in the leaves, stalks and roots of this plant, has the composition $C^{14}H^{8}O^{9}$. The tannic acid in the leaves

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has the composition $C^{14} H^8 O^9$. Of this acid no trace is found in the roots, any more than of ruberythric acid in the leaves. While the tannic acid of the *Cinchona nova* is decomposed into chinovared and sugar, according to the equation $C^{14} H^8 O^7 = C^2 H^2 O^2 + C^{12} H^6 O^5$, ruberythric acid is decomposed into sugar and alizarine in a precisely similar manner, $C^{14} H^7 O^7 = C^4 H^4 O^4 + C^{10} H^3 O^3$. The formation of ruberythric acid appears to take place in the stems of *Rubia tinctorum*. Whilst the lower parts of the stem contain yellow colouring matter, none is to be seen in the upper portion. If the stems be crushed, they acquire a red colour on exposure for some time to the air.

The quantity of ruberythric acid in the roots of madder does not amount to more than about 1 grm. in 25 lbs. of the air-dried root. The madder of the Levant contains more of this acid than that grown in Europe.

The author showed, in his previous investigation upon madder, that all the alizarine and purpurine was precipitated from an aqueous decoction of madder by neutral acetate of lead. Baryta water may be employed in a similar manner. A decoction of madder gives a violet precipitate with baryta water, which, when filtered off, and treated with moderately-strong nauriatic acid, gives a solution containing chloride of barium, whilst the alizarine and some purpurine remain behind, and may be purified by repeated crystallization.

If alizarine be placed in a bulb-tube, and ammoniacal gas be passed over it, it evolves heat and acquires a violet colour. The ammonia is driven off by heat, and the alizarine then resumes its yellow colour. If the alizarine be heated to volatilization in a current of ammonia, a little carbon remains, and a violet pulverulent sublimate is obtained, which is but slightly soluble in water. By the addition of a little ammonia, it dissolves with the colour of alizarine, and the addition of acids throws down orange-yellow flakes of this substance. Thus the following substances are contained in madder,—citric acid, pectic acid, ruberythric acid, alizarine, purpurine, sugar, the three latter bodies probably formed by the decomposition of ruberythric acid and rubichloric acid.—*Bericht der Akad. du Wiss. zu Wien*, 1852.

On the Decomposition of Ammonia by Heat, and the employment of the Gaseous Mixture thus produced in Analysis. By M. Bouet Bonfil.

The author has found, that ammoniacal gas, when passed through tubes filled with quicklime, is resolved into its elements, nitrogen and hydrogen, at a heat far below redness. In empty porcelain tubes, or in tubes filled with fragments of porcelain, the decomposition is imperfect. The author proposes to employ the mixed gases obtained by this mode of decomposition to the reduction of metallic oxides, where the nitrogen can do no harm. It is easy in this way to obtain hydrogen gas perfectly free from arsenic, antimony, carbon, &c.—*Comptes Rendus*, xxxiv. p. 588.

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On Periodic Acid and the Periodates. *By* M. LANGLOIS.

Since 1833, when the *periodic acid* was discovered by Magnus and Ammermüller, our knowledge of the combinations of this acid have received scarcely any additions except those made by Rammelsberg and Benckiser.

Periodic acid is regarded by Langlois as an acid with 5 equivs. of basic hydrogen (*acide pentahydrique*). In its salts these 5 equivs. of hydrogen are completely, or in part, replaced by metal. The acid is very deliquescent, and crystallizes in rhombic prisms, as has already been stated by Benckiser.

The acid, dried *in vacuo* over sulphuric acid, was decomposed by exposure to heat in a tube closed at one end. At 266° the crystals melted; at 392°–410° they lost all their water and 2 equivs. of oxygen, and there remained in the tube nothing but iodic acid, which is not decomposed at this temperature. The loss of weight amounted to 26·68, 26·78, 26·97, 27·36 per cent., or on the average to 26·94 per cent. If we calculated the water contained in the periodic acid at 5 equivs., it would give 26·77 per cent., which agrees well with the ascertained loss of weight. Rammelsberg, moreover, has already shown that in the salts of the alkaline earths H^5 are replaced by M^5. The acid is immediately decomposed by sulphurous acid, muriatic acid and sulphureted hydrogen. With morphine it acts like iodic acid, iodine being set free after a short time, as can be shown by means of starch-paste. It precipitates a solution of tannic acid, which iodic acid does not. Ammonia and caustic potash dissolve the precipitate, and the liquid thus formed acquires a deep red colour from the oxidated tannin. Gallic acid is not precipitated by periodic acid, but becomes similarly coloured.

Periodic acid is but slightly soluble in alcohol and æther. It is however more readily dissolved by alcohol than by æther. In such a solution it gradually changes into iodic acid, which may be readily recognised by the precipitate which it gives with nitrate of silver and by the insolubility of this precipitate in nitric acid. Periodic acid is always prepared either from the silver salt or from the lead salt.

The usual mode of procuring periodic acid from the iodate of soda is as follows:—A solution is formed of 1 equiv. of iodate of soda and 3 equivs. of hydrate of soda and periodic acid produced by passing into it a current of chlorine. If the reaction here were complete, there would be 1 equiv. of periodate of soda (IO^7, 2NaO, 3HO) and 2 equivs. of chloride of sodium; but there always remains behind a quantity, nearly one-half, of the iodate of soda employed. According to the author, it is best to use equal parts of soda and iodate of soda; the hydrate of soda is first dissolved in water, and the iodate of soda added to it, by which a solution is procured immediately in as concentrated a state as possible, the vessel containing it being placed in boiling water. The change goes on very rapidly.

From the soda salt thus procured the lead or silver salt is now to

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be prepared. The soda salt is not very soluble in water; it becomes readily soluble however on the addition of a little nitric acid, which must be free from nitrous acid. The addition of nitrate of silver or of lead throws down an insoluble salt in both cases. The formula of the periodate of silver according to Ammermüller is $IO^7, 2AgO, 3HO$.

This salt is soluble in nitric acid, and the solution deposits on evaporation orange-yellow crystals, which contain no water, and only 1 equiv. of acid instead of 2. Boiling water removes periodic acid from this salt; this solution is evaporated first in the water-bath, and afterwards *in vacuo*, to procure pure periodic acid, free from iodic acid. By Benckiser's process of decomposing the salt of lead, the periodic acid procured is always much contaminated with iodic acid. The lead salt has the formula $IO^7, 3PbO, 2HO$, and is easily prepared by mixing 1 equiv. of the bibasic soda salt with 3 equivs. of nitrate of lead. The periodic acid can also readily be procured from the baryta salt, prepared according to Rammelsberg's process. In this method, however, there is a great loss of iodine.

Bibasic Periodate of Soda, $IO^7, 2NaO, 3HO$, is the salt described by Magnus and Ammermüller. It has the composition of the acid, 2HO in the latter being represented by 2NaO. At 392° it loses no water. At a red heat it lost 6 atoms of oxygen and all its water, consisting according to four experiments of 27·04, 27·20, 26·88, 27·51 per cent., which had already been found to be the case by the discoverers of the acid. The residue has the remarkable composition which will be seen in the following equation:—

$$IO^7 + 2NaO, 3HO = IO, 2NaO, O^6, 3HO.$$

The properties of this residue render it more probable that it consists of $IO^3, 3NaO + NaI$. According to this, an iodite and iodide are produced, as in the case of chloride of lime. Its formation might be explained in the following manner:—

$$2(IO^7, 2NaO, 3HO) = IO^3, 3NaO, NaI + O^{12} + 6HO.$$

This iodite attracts water and carbonic acid from the air, and becomes covered with iodine. It is scarcely soluble in water, but is immediately coloured yellow by it, and has then a saffron and iodine-like odour; and when stirred up daily to expose it to the action of the carbonic acid of the atmosphere, it behaves exactly like hypochlorite of lime. This mass is also immediately decomposed by acids. In a strong bright red heat it gives off oxygen.

Monobasic Periodate of Soda, $IO^7, NaO, 4HO$.—Magnus and Ammermüller procured only the anhydrous salt, IO^7, NaO. The author has prepared the hydrous salt by saturating the bibasic salt with acid, concentrating the solution by a heat of 122°–140°, and drying the resulting rhombic crystals *in vacuo* over sulphuric acid. On exposure to a heat of 295°, it lost 14·47 per cent.; the above formula gives 14·40. At a red heat, the loss of water and oxygen amounted to 37·20; theory requires 36·80. The residue was neutral iodide of sodium.

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Monobasic Periodate of Potash, $IO^7 KO$.—The author procured the neutral salt of Magnus and Ammermüller, by treating a mixture of iodate of potash and potash in solution with chlorine. The salt has an acid reaction, which is what would be expected considering that it is formed by a pentahydric acid. It contains no water of crystallization. It is decomposed by heat into—

	Found.	Calculated.
Iodide of potassium	71·95	72·53
Oxygen	28·05	27·47

Periodate of Lithia is readily prepared by dissolving carbonate of lithia in periodic acid. It forms a crystalline mass, soluble in water; and at a red heat loses water, oxygen and iodine; but the whole of the latter with difficulty.

Monobasic Periodate of Ammonia, $IO^7, NH^4O, 4HO$.—A watery solution of periodic acid, when poured into liquid ammonia, immediately throws down a precipitate, which is soluble in a large quantity of water. From such a solution well-formed crystals are procured by gradual evaporation; their form appears to be the rhombic prism. They redden litmus, and are readily soluble in water to which a few drops of nitric acid have been added. Nitrate of silver throws down in this solution an orange-yellow precipitate, which is soluble in nitric acid. When the crystals of periodate of ammonia are heated in a glass tube, they are decomposed with explosion. Analysis gave—

I	53·33	1	52·58
NH^3	6·60	1	6·94

Periodate of Baryta, $IO^7, 2BaO, 3HO$, is prepared by adding baryta water to the solution of periodate of soda made by the agency of nitric acid. It appears as a white precipitate, which when dried at 212° gave 63·03 and 63·45 per cent. of sulphate of baryta; the formula gives 62·55. Rammelsberg has made known two other salts, $IO^7, 5BaO$, and $2IO^7\,5BaO, 5HO$.

The new salt of the author liberates oxygen, iodine, and water in quantities agreeing with its formula, and there remains a periodate with 5 atoms of baryta, similar to that procured by Rammelsberg, by exposing iodate of baryta to a moderate heat. This is formed in accordance with the following equation:—

$$(IO^7, 2BaO, 3HO)^2 = (IO^7, 5BaO)^2 + I^3 + O^{21} + 15HO.$$

100 parts of the salt should yield 62·30 of pentabasic periodate; 61·83 and 61·55 were obtained. That the residue is the pentabasic salt is proved by the determination of the baryta; 100 parts gave 103·88 and 103·28 of sulphate of baryta; theory requires 103·04.

Periodate of Strontia, $IO^7, 2SrO, 3HO$, is procured by treating strontia water in the same manner as directed above for baryta water. In the determination of the strontia, 59·20 of sulphate of strontia were obtained; the formula gives 58·64. The salt has therefore the same constitution as the baryta salt.

Periodate of Lime, $IO^7, 2CaO, 3HO$, was obtained by the author by pouring nitrate of lime into a solution of monobasic periodate of

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soda. The white precipitate thrown down has a crystalline appearance under the microscope. On exposure to heat, it behaves like the two preceding salts. It gives 44·93 of sulphate of lime; calculation gives 45·35.

Periodate of Magnesia, IO^7, 2MgO, 3HO + 9HO.—This salt cannot be prepared by the double decomposition of a soluble salt of magnesia and the monobasic periodate of soda, on account of its great solubility. It is prepared by pouring periodic acid upon carbonate of magnesia. This salt appears under the microscope in small prismatic crystals, which at 212° lose 9 equivs. of water, and then still contain 3HO, in which state the salt has the same composition as most other periodates. On exposure to a red heat, there remains 16·92, 16·60, 16·32 per cent. of magnesia; and on heating it to redness with potash, an iodide of potassium is procured, which gives 72·94 and 72·41 of periodic acid. The formula IO^7, 2MgO, 3HO requires—

Magnesia	16·54
Periodic acid	72·72

Periodate of Zinc, IO^7, 4ZnO, HO and $2IO^7$, 3ZnO, 7HO, is obtained by treating hydrated carbonate of zinc with periodic acid. The salt produced has the appearance of a granular powder, and contains no carbonate of zinc if the periodic acid be a little in excess. Heated to 212°–248°, this salt undergoes no change. It is readily soluble in distilled water to which nitric acid has been added. The solution gives a yellow precipitate with nitrate of silver. The precipitate is completely soluble in nitric acid. The salt is soluble in water on the addition of a little acid. By evaporation, the sesquibasic salt, $2IO^7$, 3ZnO, 7HO, is obtained. The tetrabasic salt gives on analysis—

IO^7	51·23	1	51·96
ZnO	46·26	4	45·49
HO	..	1	2·55

The protoxides of iron and manganese reduce periodic acid into iodic acid; iodates of the oxide of manganese and peroxide of iron are precipitated.

Periodate of Lead, IO^7, 3PbO, 2HO.—This salt is obtained by pouring a solution of nitrate of lead into a solution of bibasic periodate of soda. The precipitate has a crystalline appearance under the microscope. It is readily soluble in water which contains a little nitric acid. When dried *in vacuo*, the salt can be heated to 248°–266° without loss of weight. The water of crystallization first begins to disappear when the decomposition of the salt commences. When heated in a tube, it loses water, oxygen and iodine, and there remains the basic iodide of lead, PbI, 5PbO. The loss at a red heat amounted to 25·67, 25·78, 25·40 for 100 parts of salt; by calculation from the equation $(IO^7\,3PbO, 2HO)^2 = (PbI, 5PbO) + O^5 + I + 4HO$, the loss should be 26·40 per cent. Periodate of lead gave 84·30, 83·51, 83·98, 84·50, 83·96 per cent. of sulphate of lead. The average, 84·05, comes sufficiently near to the quantity

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calculated according to the formula IO^7, 3PbO, 2HO = 84·70. Analysis gave the following numbers (the water not directly determined):—

PbO	61·88	3	62·49
IO^7	33·54	1	34·13
HO	..	2	3·38

Periodate of Copper, IO^7, 4CuO, HO, procured by the addition of sulphate of copper to monobasic periodate of soda, or better, and with less loss, by treating carbonate of copper with periodic acid in slight excess, has the following composition:—

IO^7	51·90	1	52·16
CuO	45·54	4	45·27
HO	..	1	2·57

The Monobasic and Bibasic Periodates of Silver have also been examined by the author. The latter crystallizes in rhombic prisms with 2 equivs. of base and 3 of water. In other respects the examination has added nothing new to the facts ascertained by Magnus and Ammermüller.

Combinations of Alkaloids with Periodic Acid.—Periodic acid unites with difficulty with organic bases; nevertheless many combinations may be successfully prepared by dissolving the bases in alcohol and saturating them with acid.

Periodate of Quinine, $(C^{38}H^{24}N^2HO)IO^7 + 22HO$.—On attempting to combine quinine, recently precipitated by ammonia, with periodic acid, it will be found that even when the alkaloid is in excess the acid will not be completely neutralized. After standing a short time over sulphuric acid *in vacuo*, the surface will be found covered with a substance of an oily appearance, which possesses the tenacity of turpentine. It afterwards falls to the bottom, and forms crystals, which are decomposed with explosion when heated on platinum foil, and leave behind a small quantity of carbon. They are readily soluble in water; silver salts produce a yellow precipitate in this solution; and this precipitate is soluble in nitric acid, from which it appears that the periodic acid has undergone no decomposition. But after some time these crystals are decomposed; so that by this process no decisive results are arrived at.

The method already above mentioned appears to be better. The acid and base are dissolved, each by itself, in alcohol, and the one solution saturated with the other. It is allowed to evaporate at 86°–104°, by which means crystals are obtained, which are sparingly soluble in water, but are readily dissolved on the addition of a little nitric acid. Ammonia and nitrate of silver throw down precipitates in this solution. The yellow precipitate is soluble in nitric acid; no iodic acid has therefore been formed by the oxidation of the base. Analysis gave—

IO^7	25·36	1	26·05
$C^{38}H^{24}N^2HO$.....	46·25	1	45·73
HO	..	22	28·22

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Periodate of Cinchonine.—Cinchonine does not behave exactly like quinine with periodic acid. It never completely saturates this acid, and the liquid always reddens litmus. If the solution be concentrated *in vacuo* over sulphuric acid, similar phænomena occur as with quinine; a turpentine-like mass is first of all obtained, which afterwards becomes crystalline. The crystals soon become yellow, and the periodate is reduced to iodate, more readily than with quinine.

If we make use of alcoholic solutions of periodic acid and cinchonine, pouring the former into the latter, as in the second process given above for quinine, a neutral liquid is obtained, and by evaporation at a very moderate heat, short prismatic crystals are formed, which are immediately changed when they are not protected from the air by the mother-liquor. They become yellow in the air, and the periodic acid is entirely reduced to iodic acid, in the course of some time.

Morphine behaves towards periodic acid as towards iodic acid. Iodine is set free, and a part of this iodine combines with the morphine to form a protiodide.

Strychnine, treated directly or in an alcoholic solution with periodic acid, furnished numerous crystals by concentration *in vacuo*. They are six-sided prisms, terminated by a four-sided pyramid. When heated on platinum foil, they burn without explosion, and leave behind a small black residue. Nitrate of silver throws down a yellow precipitate in their aqueous solution; this precipitate is perfectly soluble in nitric acid. The solution of periodate of strychnine never becomes red like that of the iodate of strychnine.

Brucine unites more readily with periodic acid when dissolved in alcohol, than when brought into contact with it as a powder. By evaporation at 86°–104°, beautiful colourless needles are obtained, which when heated on platinum foil are decomposed with a slight noise, and only leave behind a trace of carbon.

Veratrine unites with periodic acid when a solution in alcohol is used, and requires only a small quantity of acid for its saturation. If the solution be evaporated in a warm atmosphere, a butyraceous substance is obtained, which very soon becomes hard and resinous, and encloses a number of microscopic crystals. By testing with nitrate of silver, it may be readily ascertained that the periodic acid has undergone no change.—*Ann. de Chim. et de Pharm.*, xxxiv. p. 257.

On the new Compound of Mercury of Sobrero *and* Selmi. *By* MM. Werther *and* Brückner.

Werther attempted to prepare the compound of mercury which Sobrero and Selmi* stated that they had obtained as a precipitate from an alcoholic solution of chloride of mercury by means of potash. He did not succeed in procuring a precipitate containing a group of organic elements. Brückner obtained the same negative result.—*Journ. für Prakt. Chem.*, lv. p. 253.

* Chem. Gaz., vol. ix. p. 325.

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Sulphur in Pyroligneous Spirit. *By* REUBEN PHILLIPS*.

During the course of some recent researches, I was occasionally perplexed by the anomalous appearance of sulphur; and the following experiments were made to ascertain its source. As I cannot find that any one has yet noticed the existence of sulphur in pyroligneous spirit, perhaps these experiments may be acceptable to those who use pyroligneous spirit for fuel.

About 6 grs. of hydrate of soda were placed in a silver crucible, capable of containing about $1\frac{1}{2}$ oz. of water. The soda was then fused, and the crucible inclined in various positions so as to line it with soda. The spirit to be tested was placed in a glass spirit-lamp holding nearly $\frac{3}{4}$ of a volume ounce†, and then the flame was driven into the crucible by means of a blowpipe, which was fed with air from a metallic vessel in which it had been strongly condensed. After the lamp-full of spirit had been thus burnt and the crucible had become cool, sufficient water was added to dissolve the saline matter; the solution was then filtered, an excess of hydrochloric acid added, and then a little chloride of barium. All the samples of pyroligneous spirit which I have obtained, when treated by this process, afforded an abundant precipitate of sulphate of baryta.

I satisfied myself, by a number of experiments with alcohol, that the process would not yield sulphur, unless sulphur existed in the products of the combustion of the spirit.

12 vol. oz. of nearly colourless pyroligneous spirit were mixed with 20 oz. of water. After some hours the mixture was thrown upon a filter; the fluid that passed was scarcely at all milky, and but little troubled by a further addition of water. By this treatment nearly 5 vol. drms. of a slightly yellowish oil were separated. The filtered fluid was now rectified by a continued fractional distillation, and I thus obtained $5\frac{3}{4}$ vol. oz. of perfectly colourless pyroligneous spirit, having a specific gravity of about 0·867. This spirit was now mixed in a retort with powdered chloride of calcium; on cooling, a thick mass was obtained intermixed with clear fluid. I did not saturate the fluid with chloride of calcium, thinking that an excess of chloride of calcium might render the separation of the sulphur compound more difficult. The retort was then placed in a water-bath. The distillation proceeded rapidly for a few minutes, but soon became very slow; the heat was however kept up for about $2\frac{1}{2}$ hours; $2\frac{1}{2}$ vol. oz. were obtained. 2 oz. of water were now added to the materials in the retort, and the distillation continued; the second product amounted to 7 vol. drms.

The product of the first distillation, namely the $2\frac{1}{2}$ vol. oz., on being tested, gave as much sulphate as so much crude spirit. The second quantity, namely the 7 vol. drms., gave about a third of this quantity of sulphate of baryta. It now follows that the sulphur compound of pyroligneous spirit is not separated with the oily matter;

* Communicated by the Author.

† To prevent obscurity and circumlocution, I use the term *volume ounce*, or *vol. oz.*, as equivalent to the *volume of an ounce of distilled water*.

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and also, it may be confidently predicted, that the spirit can be obtained free from sulphur by a continued repetition of Sir R. Kane's chloride of calcium process.

An attempt was made to separate the sulphur by distilling pyroligneous spirit from a mixture of hydrate of potash and oxide of lead; but the distilled fluid contained as much sulphur as ever.

Sulphur can also be found in pyroligneous spirit by decomposing it in a retort with strong nitric acid.

A mixture of pure lamp-black and hydrate of soda, placed on a platinum capsule, and ignited for about twenty minutes by a lamp fed with pyroligneous spirit, gave rather a strong reaction of sulphate of soda. Consequently it is necessary to regard this source of sulphur in the incineration of organic matters.

7 Prospect Place, Ball's Pond Road,
June 8, 1852.

On a Combination of Sulphur, Nickel and Bismuth.
By G. Werther.

Werther has examined a mass of interlaced bismuth crystals, which was formed in the purification of the bismuth of commerce. The purification was carried on according to the prescription of the Prussian Pharmacopœia (sixth edition), in which 8 parts of bismuth, 1 part of dried and purified carbonate of soda, and ½ part of sulphur are melted together. On pouring off the fluid metal in the usual process for effecting the crystallization of the bismuth, crystals were found on the sides of the crucible, the form of which could not be determined. They possessed a strong metallic lustre, like that of bismuth, but with less of a reddish tinge. Their specific gravity was 9·15 at 63° F. in the pulverulent state. They are friable and brittle, but not to the same degree as bismuth. Before the blowpipe, all the reactions of sulphur, bismuth, and nickel were readily obtained. The analysis of this compound gave—

Bismuth	87·74	86·80	12	87·67
Nickel	10·12	10·23	5	10·13
Sulphur	..	2·28	2	2·20

From this the author derives the formulæ $2NiS+3NiBi^2$, or $NiS^2+4NiBi^3$. The formula $2BiS+5NiBi$ appears to him less likely to be correct.—*Journ. für Prakt. Chem.*, lv. p. 227.

Malic Acid contained in the Berries of Hippophaë rhamnoides.
By Prof. Erdmann.

The berries of *Hippophaë rhamnoides*, when allowed to dry in the open air, acquire a considerable crystalline coating of malic acid. From 15 to 20 grms. of berries, so large a quantity of crystallized malate of lead was procured as to enable the author to determine the nature of the acid. The author considers these berries to be the richest existing source of malic acid.—*Journ. für Prakt. Chem.*, lv. p. 191.

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Chemical Examination of the Flower-Buds of Capparis spinosa. *By* MM. Rochleder *and* Hlasiwetz.

The authors have made some experiments with the capers prepared with vinegar and salt in the state in which they occur in commerce, and have found in them rutic acid, together with a substance belonging to the pectic acid series. The capers had as much water poured over them as sufficed to cover them, were allowed to stand for some hours, and then put into a sieve and pressed through with the hands. This process, the object of which was to remove the large quantity of vinegar and salt which was contained in the capers, was twice repeated.

The capers were then exhausted with boiling water, the decoction concentrated as much as possible, and then separated from the capers by a sieve, and these boiled once more with water.

The two decoctions, when mixed, were allowed to stand quiet in a cool place for twenty-four hours. After this time a large quantity of voluminous flakes, of a light yellow or nearly white colour, were found swimming in a brown liquid. This liquid, with the contained flakes, was then put upon a filter, the brown mother-liquor drained off, and the flakes collected and dried. Under the microscope the dry mass appeared to consist of interwoven aciculate crystals. It was dissolved in boiling alcohol, and the solution filtered while hot. There remained on the filter a small quantity of a gelatinous substance. The filtered alcoholic liquor was mixed with a fourth of its volume of water, and the alcohol evaporated in the water-bath. The residue cooled into a jelly, which was allowed to drain on a filter, and then pressed in blotting-paper. This pressed mass was dissolved in the requisite quantity of boiling water, the boiling liquid filtered on a hot funnel, and then allowed to cool. It stiffened on cooling into a gelatinous mass of microscopic crystals. By three or four repeated crystallizations, the substance was obtained pure.

The substance, when crystallized from water, forms small interwoven needles of a white colour, with a tendency towards sulphur-yellow; it crystallizes from alcohol in somewhat large needles of a pale sulphur-yellow colour. This colour is proper to the substance. When not in a perfectly dry state, this yellow colour is increased by exposure to air impregnated with ammonia.

This body is very sparingly soluble in cold water; even boiling water dissolves very little of it, and on cooling, nearly the whole quantity dissolved falls down. Alcohol dissolves more of it than water, and the hot saturated solution remains clear on cooling, the substance crystallizing only on the evaporation of the alcohol. Æther also dissolves a small quantity of this body.

In alkaline fluids, such as potash-, soda-, ammonia- or baryta-water, it is dissolved readily. All these solutions have the yellow colour of the neutral chromate of potash. By exposure to the air, these solutions absorb oxygen, and acquire a dark brown colour.

A watery solution of the substance acquires an intense green

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colour on the addition of a solution of perchloride of iron. An alcoholic solution, mixed with an alcoholic solution of sugar of lead, gives a precipitate of a beautiful chrome-yellow colour.

Aqueous solutions of this body gradually reduce the oxides of the precious metals from their solutions at ordinary temperatures. The same thing takes place instantly at the boiling-point of water.

This body behaves in a peculiar manner towards acids. In hot acetic acid it is dissolved in great quantity. On cooling, only a part of the dissolved portion is thrown down; the other part separates as the acetic acid evaporates; this is best done in a warm place. In this manner prisms grouped in a cauliflower-form are obtained.

When tolerably concentrated mineral acids are poured over it, this substance instantaneously acquires a citron-yellow colour; on the application of heat, it is dissolved with the same colour. On heating, citron-yellow flakes are separated, which appear under the microscope as four-sided prisms grouped in a stellate form. On pouring cold water over them, the yellow colour immediately disappears, and the flakes acquire a pale yellow colour, and on heating are dissolved with the same colour. The flakes which separate on cooling are pale yellow, and appear under the microscope as stellate groups of needles. But if the deep yellow crystals obtained by means of acids, or those changed to pale yellow by the action of water, be dissolved in liquid ammonia, and the substance separated by a diluted acid, it appears again with its original properties, such as it possessed before being treated with acids. This property of becoming yellow appears to depend on an abstraction of water.

Cold nitric acid gives the substance a yellow colour; on being heated, it dissolves it with a yellow colour and evolution of gas. It cannot be obtained unchanged from this solution.

In concentrated sulphuric acid it is dissolved with an olive-green colour.

At a temperature of 212°, this substance undergoes no change; at a higher temperature, it melts, and cools into a brittle transparent resin, which, when pounded, gives a pale yellow powder. If the temperature be raised above the melting-point, decomposition commences, the melted mass becomes brown and puffs up, and there remains a bulky coal, whilst a proportionately very small quantity of fluid products distils over. Exactly the same phænomena occur if the distillation be carried on in a stream of ammoniacal gas.

All these properties, and the behaviour of this body with various reagents, agree with the properties and reactions of rutic acid, which was discovered by Weiss in the herb of *Ruta graveolens*, and has since been more closely investigated by Bornträger*.

The numbers obtained by analysis, with those procured by Bornträger by the analysis of rutic acid, are given below. The substance was dried at 212°:—

	The Authors.	Bornträger.				
Carbon.....	50·15	50·34	50·27	12 =	900·0	50·00
Hydrogen ..	5·70	5·55	5·54	8	100·0	5·55
Oxygen	44·15	44·11	44·19	8	800·0	44·45

* Chem. Gaz., vol. iii. p. 385.

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Bornträger prepared the lead salt of rutic acid, and found it to be composed according to the formula $C^{12} H^6 O^6 + PbO$. The lead salt, procured by the authors by precipitating a solution of rutic acid in spirit of wine with an alcoholic solution of sugar of lead, gave the following numbers on analysis, the substance employed being dried at 212° :—

Carbon	28·75	36	= 2700·0	28·85
Hydrogen	3·09	22	275·0	2·95
Oxygen	23·54	22	2200·0	23·51
PbO	44·62	3	4183·5	44·69

The formula $C^{36} H^{22} O^{22} + 3PbO$ is to be considered as $(C^{12} H^8 O^8, PbO) + 2(C^{12} H^7 O^7, PbO)$.

The liquid from which the rutic acid had been separated contained also a body of the pectic acid series. The decoction of the capers, from which the rutic acid crystallizes on cooling, is of a brown colour, owing to the presence of a small quantity of a resinous substance. This liquid is evaporated in flat dishes at a temperature below boiling until it acquires the consistence of weak syrup. Impure rutic acid of a brown colour is separated in small quantity. The mass is placed on a linen filter, and the liquid which passes through mixed with twice its volume of alcohol. A gelatinous matter is separated, so that the liquid becomes solidified. It is then heated to the boiling-point, by which the gelatine is drawn together and separated by filtration from the liquid.

This gelatinous substance is soluble in water, insoluble in alcohol, and is precipitated from its watery solution by a solution of sugar of lead in voluminous gelatinous flakes. It contains a small quantity of vegetable mucilage, which may be converted into sugar by boiling with diluted acids. On burning, a large quantity of ashes is left.

The substance analysed was not obtained perfectly pure. The calculated formula is only meant to show that this body should be arranged in the series of pectine compounds. It was dried at 212°. The ash is deducted :—

Carbon	35·74	56	= 4200·0	35·90
Hydrogen	5·99	56	700·0	5·98
Oxygen	58·27	68	6800·0	58·12

$C^{56} H^{56} O^{68}$ crude gelatine $= C^{28} H^{21} O^{25}$, pectous acid, $+ C^{28} H^{19} O^{27}$, hyperpectic acid $+ 16$ water.

In order to purify the gelatine, its aqueous solution was mixed with muriatic acid, boiled, the gelatine precipitated with alcohol, and washed out with alcohol. To render the washing as perfect as possible, the gelatine precipitated with alcohol was placed on linen and pressed out, dissolved in water, precipitated with alcohol, and again pressed between linen; and this process repeated until the alcohol was no longer rendered turbid by the addition of a solution of nitrate of silver. The gelatine, thus purified, was dried at 212°, and submitted to analysis. There was obtained—

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Carbon	41·16	28	= 2100·0	41·27
Hydrogen	5·66	23	287·5	5·65
Oxygen	53·18	27	2700·0	53·08

$C^{28} H^{23} O^{27}$, purified gelatine, $= C^{28} H^{21} O^{25}$, pectous acid $+ 2$ water.

It is not without interest to observe the presence of this substance belonging to the pectic series in the flower-buds, as its occurrence in the fruit is so frequent. The sepals of the capers are covered with white points, which might be taken for wax at the first glance. These points consist of rutic acid; they disappear on being treated with hot water, which dissolves the rutic acid.

The properties of rutic acid agree in many points with those of the weak acids which are met with in the lichens. The property possessed by rutic acid of forming yellow compounds with alkalies and alkaline earths, which become brown by absorption of oxygen on exposure to the air, and its properties of giving a green colour with salts of the peroxide of iron, and of forming yellow insoluble compounds with oxide of lead, render it probable that rutic acid is allied to the tannic acids which occur in the *Rubiaceæ*.

These acids, under the influence of powerful agents, are changed into other combinations, which contain less carbon and hydrogen than the acids. Whilst the acids contain 14 equivs. of carbon to 8 equivs. of hydrogen, in these derived compounds there are 12 equivs. of carbon and 6 equivs. of hydrogen, united with 5 or 6 equivs. of oxygen. These acids may be considered as conjugate compounds of a hydrate of carbon with a body possessing a constitution exactly like that of rutic acid. The properties of these acids, the faculty of forming yellow insoluble salts with oxide of lead, soluble salts with alkalies, and green salts with peroxide of iron, would evidently be best explained on the assumption that they are conjugate compounds of bodies resembling rutic acid with a carbohydrate.

The water with which the capers were freed from the greater part of their vinegar and salt contained nearly the whole of the substance to which the capers owe their peculiar odour.

The water in which 10 lbs. of capers had been washed was distilled in the sand-bath until a third part of it had gone over. The resulting fluid contained acetic acid, which could be easily removed. There appeared to be no trace of any fluid oil on the water, which possessed a penetrating, acrid and alliaceous odour; there were, however, flakes of a solid substance floating on the water and lying on the bottom of the vessel; but they scarcely amounted to more than a grain in weight, and were consequently in too small quantity to render an examination of them possible.—*Sitzungsb. der Akad. du Wissensch. zu Wien*, Jan. 1852.

Examination of the Urine in Dropsy. *By* C. Neubauer.

C. Neubauer of Wunstorf has examined the urine of a scrofulous man, aged twenty, who was suffering from tubercles in the lungs

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and intestines. The urine was of a brownish colour, and of 1·011 spec. grav. It contained—

	In 20 grms.	In 100 grms.
Water	19·470	97·350
Phosphate of lime, Phosphate of magnesia, Sulphates	0·015	0·075
Albumen	0·150	0·750
Extractive, Urea, Uric acid (traces), Salts of ammonia (chloride?), Mucus of the bladder	0·356	1·825
	19·999	100·000

Berzelius has already observed, with regard to anasarca, that at the commencement of the complaint the albumen only occurs in the urine in small quantity. It is then only to be recognised by corrosive sublimate.

During the progress of the disease, when not only are the serous fluids poured into the urinary passages, but the kidneys also secrete an albuminous liquid, the albumen may be recognised by less delicate reagents, such as nitric acid, alum, &c.; at last it may even be coagulated by boiling. In proportion to the increase of albumen, the quantity of uric acid and urea diminishes, until at length they entirely disappear.

In the urine examined by the author, the albumen readily coagulated on boiling, and became completely separated by this process, so that the weight could be determined. The extremely small quantity of urea and uric acid agrees well with this large proportion of albumen. The nitrogen which had become useless in the body, was now no longer, as in health, separated by the kidneys in the form of the two above-mentioned bodies, but as albumen, which was also present with the serous fluids in the urine.—*Archiv der Pharm.*, lxix. p. 298.

On a new Plastic Material for forming various Objects. *By* Prof. Purkinje.

5 parts of sifted whiting are mixed with a solution of 1 part of glue. When the whiting is worked up into a paste with the glue, a proportionate quantity of Venetian turpentine is added to it, by which the brittleness of the paste is destroyed. In order to prevent its clinging to the hands whilst the Venetian turpentine is being worked into the paste, a small quantity of linseed-oil is added from time to time. The mass may also be coloured by kneading in any colour that may be desired. It may be pressed into shapes, and used for the production of *bas-reliefs* and other figures, such as animals, &c. It may also be worked by hand into models, during which operation the hands must be rubbed with linseed-oil; the mass must also be kept warm during the process. When it cools

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and dries, which takes place in a few hours, it becomes as hard as stone, and may then be employed for the multiplication of these forms.—*Gewerbebl. aus Wurtemb.*, 1852, p. 45.

ANALYTICAL CHEMISTRY.

On the Separation of Nickel and Cobalt.

TO WILLIAM FRANCIS, ESQ.

MY DEAR SIR,—In the Chemical Gazette, vol. v. pp. 362–372, you published a translation of H. Rose's excellent and elaborate memoir "On the Separation of Nickel and Cobalt," with some valuable remarks appended by our mutual friend Mr. T. H. Henry, which notice forms the most complete monograph we possess on this subject.

It would be but a waste of the space of your Journal, and of your readers' time, to recapitulate the searching examination of the processes of Phillips, of Laugier, and of Liebig, by the chemist of Berlin, and the imperfections of each pointed out by him; nor is it requisite for my present purpose to do more than to recal to your readers' memories, that the perfectly successful and unobjectionable plan of H. Rose consisted in thoroughly saturating a very dilute solution of the mixed metals with chlorine gas, and digesting an excess of precipitated carbonate of barytes in this chlorinated solution for some twenty-four hours, at the expiration of which time the whole of the cobalt is precipitated as peroxide, but none of the nickel; after which, by filtration, and the common treatment requisite to separate the barytic earth, the oxides of nickel and cobalt can be separately procured in a state of perfect purity. Mr. T. H. Henry ingeniously suggested the substitution of bromine for chlorine, as getting rid of the annoyance caused by the latter gas, especially in private laboratories attached to dwelling-houses; but bromine vapours to many, certainly to myself, are more annoying than chlorine; besides, I believe it is a failing common to chemists, to look on a reagent which has once been very rare and expensive, as too sacred an article to be used for ordinary analytical purposes; and I doubt whether, owing to the prevalence of this feeling, Mr. Henry's modification of Rose's process is generally adopted.

Having to separate cobalt and nickel, when analysing a speiss, a short time since, I successfully adopted a modification of Rose's process, which gets rid of all the nuisance arising from the escape of chlorine, and saves both time and trouble, by the employment of a very dilute solution of chloride of lime acidulated with sulphuric acid. I used it thus. After separating the bismuth, copper, arsenic, iron, &c., which the speiss contained, by the usual methods, I dissolved one-half the weight of the speiss employed of chloride of lime in water, and plentifully diluted this solution, adding to it very dilute sulphuric acid slightly in excess, it being requisite that no free lime should remain in solution, nor undecomposed chloride, as either would decompose the nickel salt; then, this solution, con-

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taining chlorine, hypochlorous acid, or whatever else it may, is poured into the solution of the mixed metals, also much diluted, as directed by Rose, and to them a thin cream of carbonate of lime (common whitening is the best) is added in excess, and the mixture digested together for twenty-four hours at the least, or for days if it be inconvenient to proceed with the analysis, when the decomposition of the cobalt salt is completely effected; and the oxide of this metal, mixed with the excess of carbonate of lime, may be separated from the solution of nickel. Lime is not so readily separated from the cobalt and nickel oxides as barytes is, carbonate of ammonia, added to an ammonio-calcareous solution of either, always precipitating a small portion of the oxide of each, probably as a double carbonate; and although oxalate of ammonia is free from this objection, oxalate of lime is sometimes an unmanageable precipitate; I therefore prefer the use of sulphureted hydrogen, passed in excess through the ammoniacal solution, as being an easy method of precipitating both metals; this is especially the case with nickel, the sulphuret of which metal may frequently be treated with dilute hydrochloric acid without being in the least acted upon, and thus prevent the formation of any carbonate of lime; moreover, after this acidulation, it is far more readily filtered than before; I say, frequently, because I have known it attacked and partly redissolved by the acid; why, I don't know, but probably from the acid used being insufficiently diluted. These observations also apply to the sulphuret of cobalt, the only difference between them being, that the sulphuret of this metal appears to be more readily acted on by acids than is the sulphuret of nickel.

Believe me, my dear Sir,
Yours truly,

Putney, June 15th, 1852. J. Denham Smith.

P.S. A few words on the precipitation of nickel. In practice, I have always found that all gelatinous precipitates, when potash or soda has been the reagent employed, retain most obstinately a portion of the alkali, and thus vitiate the results. Oxide of nickel is especially subject to this objection, the fixed alkalies being its usual precipitants; moreover, it is not very easy to obtain oxide of nickel, by the ignition of the hydrate, free from peroxide. To avoid both of these inconveniences, I have adopted the following plan with success:—The solution containing only the nickel, excepting alkaline or ammoniacal salts, is to be evaporated to dryness, then powdered finely, together with a little more than its own weight of anhydrous carbonate of soda, and ignited in a platinum or silver crucible; it readily fuses at a red heat, and the fused residue, when carefully washed with boiling water and ignited, yields pure oxide of nickel of a pale dirty green tint. It is better for the nickel to exist as sulphate, rather than as chloride. This method has the further advantage of being more manageable than the plan of precipitating, which, from the necessity of using very dilute solutions, and the bulky nature of the precipitate, occupies much space and time, as well as being more troublesome than the mode described above.—J. D. S.

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THE CHEMICAL GAZETTE.

No. CCXXXIV.—July 15, 1852.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Peroxide of Silver. *By* F. MAHLA.

THE substance usually called peroxide of silver was discovered by Ritter in the year 1804, and prepared by him in the only way by which it can be procured at the present day, if we except the mode of preparation proposed by Schönbein, by means of the still very problematical body denominated *ozone*. It is formed, as is well known, by passing a galvanic current through a solution of nitrate of silver, when it makes its appearance at the positive pole in the form of beautiful prisms of a metallic lustre, whilst at the negative pole metallic silver is reduced in a crystalline form. After Ritter, Von Grotthuss was the first who occupied himself with this substance, without however adding anything to the facts already known, except that it was dissolved by ammonia with a rapid evolution of nitrogen gas, so that it possessed the power of decomposing ammonia at ordinary temperatures. More recently, Fischer made known various observations upon it, namely, that it is dissolved by nitric acid with a brown colour and without the evolution of oxygen, and that it has the property of detonating on being heated.

The first experiments to ascertain its quantitative composition were made in 1843 by Wallquist*. He supposed the probable composition to be AgO^2, as he found in 100 parts—

Silver	87·23	1	87·11
Oxygen.....	12·77	2	12·89

A year later, however, Fischer remarked† that this substance, even after the most complete washing, disengages red fumes of nitrous acid on being heated, so that Wallquist's analysis could not be correct; and he afterwards published a paper on the subject, in which he endeavoured to make it probable that this so-called peroxide contained not only nitric acid, but water also,—that it was a hydrated compound of nitrate of silver with peroxide of silver, and that its composition was expressed by the formula $4AgO^2 + AgO\,NO^5 + 2HO$. He explains the property already mentioned of producing a sort of explosion on being heated, as arising from the loss of water, but he did not observe any evolution of hydrogen gas.

These contradictory statements have induced the author to make

* Chem. Gaz., vol. ii. p. 323. † *Ibid.*, vol. iii. p. 97.

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a new investigation of this substance in Wöhler's laboratory. For its preparation two things are necessary, a Grove's battery and a solution of pure neutral nitrate of silver. As, during the action of the current, the resulting crystals of silver and peroxide have a great tendency to intermix, and it is difficult in consequence to obtain the peroxide free from metallic silver, their complete separation was effected by placing in the large cup containing the solution of silver a second smaller cup, in such a manner that its margins were below the surface of the fluid, so that the outer fluid surrounding the small cup and that within it were continuous.

The negative pole dipped into the outer solution, the positive pole in the inner, both consisting of thick platinum wire; the formation commences instantaneously, and proceeds very rapidly, particularly on the employment of a current produced by very strong nitric acid.

From time to time the crystals of peroxide must be gently detached from the wire, as otherwise they grow over the margins of the small cup, and begin to unite with the arborescent crystals of the reduced silver. In contact with this, they disappear on the interruption of the galvanic current, and are again dissolved with it, forming a nitrate. It is easy, by this process, in the course of a few hours, to procure several grammes of pure peroxide. The rapidity with which it is formed in the most beautiful crystals is very wonderful. With a sufficiently concentrated solution and a strong galvanic current, crystals are procured of the size of small peas. As long as there is not much free acid in the solution, no gas is evolved at either pole in this process; but when much acid has been set free, oxygen gas begins to be evolved at the positive pole, and the formation of the peroxide, which is then separated in a powdery form, becomes greatly diminished in quantity. When this period is passed, it sometimes also occurs, that the metal collecting at the negative pole no longer acquires the beautiful silver-white colour, but appears deep black, which colour is also communicated to the previously separated white metal. This colour however disappears as soon as the current is interrupted; the black metal then again becomes white. The form of the peroxide is an octahedron, and apparently belonging to the regular system. Notwithstanding their lustre, they are curved, and consequently not suited for accurate measurement. Sometimes also they have terrace-like cavities in their surfaces, and frequently a large number of octahedra are grouped together in the form of a long prism in the direction of the principal axis, as occurs in the case of native silver. It is consequently often procured in slender prisms, frequently an inch long, which at the first glance appear to belong to a totally different system of crystallization. The statement of Grotthuss, that it crystallizes in tetrahedrons, must be founded in error, for the author never obtained it in this form. The crystals have a grayish-black colour, and a strong dark metallic lustre. They are very brittle. Their specific gravity is 5·474.

On being heated to 230°, this peroxide evolves pure oxygen gas,

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with a sort of slight explosion, whilst the crystals fall to powder. If it be employed for this purpose in the form of a powder, it is thrown into such agitation that it overflows, and is projected out of the tube. If the residue be heated, it evolves red fumes of nitrous acid, and becomes changed into white metallic silver. This substance remaining after exposure to a heat of 230°, is a mixture of oxide of silver, AgO, and nitrate of silver, which latter may be extracted by water, whilst the oxide of silver remaining after this no longer evolves chlorine with muriatic acid, or nitrogen with ammonia.

The peroxide of silver is converted by sulphuric acid into the usual silver salt, oxygen being evolved. With colourless concentrated nitric acid it forms a red solution, which, however, on being heated, evolves oxygen gas, and becomes changed into the common salt of the oxide of silver. It undergoes the same change without evolution of oxygen, by the action of nitric acid containing nitrous acid. With a solution of oxalic acid, it causes, on the application of a gentle heat, a rapid evolution of carbonic acid, and becomes changed into white oxalate of silver. With muriatic acid it forms white chloride of silver, with evolution of chlorine. It is dissolved by ammonia with a brisk evolution of nitrogen gas. This decomposition is so violent, that the crystals are driven about in the solution like rockets. Hydrogen gas at ordinary temperatures has no influence upon it; on the application of the least heat, however, it is immediately reduced in this gas with a slight explosion. In peroxide of hydrogen it is changed into metallic silver, with a violent foaming evolution of oxygen gas.

It was probable that this substance was true peroxide of silver, which, however, in consequence of the rapid formation and enlargement of the crystals, held nitrate of silver mechanically enclosed, the decomposition of which gave the red fumes on heating. Moreover, Fischer had already observed, and L. Gmelin confirms it, that all the nitrate of silver cannot be got rid of even by the most careful washing. The author convinced himself of the correctness of this statement, for he found that well-washed crystals of peroxide, reduced to very fine powder, on being washed, furnished nitrate of silver continually, although in diminishing quantities, whilst at the same time a slight evolution of oxygen gas always took place. This washing was performed by decantation in a glass vessel, in order to prevent the decomposing influence of a paper filter. This decomposition is still more rapidly effected by hot water. Nevertheless it did not appear to be possible in this manner to effect the complete decomposition into nitrate of silver and a residue of pure peroxide. When the residue of one day's washing is analysed, it is found to contain 81·698 per cent. of silver; after two days' washing it contains 82·78 per cent.; after three days, 83·299 per cent. The pure peroxide must consequently contain 87·11 per cent. of silver. From this we may perhaps explain the result obtained by Wallquist, who appears to have succeeded in perfectly separating the compound in the above way, and to have employed the pure peroxide for his analysis, although the constant evolution of oxygen gas

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observed by the author does not agree with this. Moreover, this residue always gave off red fumes on the application of heat. It appears therefore that this substance is truly a compound of peroxide with nitrate of the oxide of silver.

For analysis, the entire crystals, well washed, were dried, partly in an air-bath at a temperature of 95° F., and partly at the ordinary temperature over sulphuric acid, until the weight remained constant.

For the Determination of the Nitrogen, two methods were adopted. In one process, the property possessed by ammonia of decomposing and dissolving the peroxide of silver with evolution of nitrogen gas, was turned to account. The solution was boiled with pure baryta-water free from nitric acid, then filtered off, and the filtrate saturated with carbonic acid. This solution was now evaporated to dryness, in order to separate the carbonate of baryta, which had been dissolved in the excess of carbonic acid; the residue again taken up by water, and then the baryta existing in the solution as nitrate thrown down with sulphuric acid. The sulphate of baryta was then filtered off, heated to redness, weighed, and the nitrogen calculated therefrom. For this investigation 3·3099 grms. of peroxide were employed, and 0·4525 grm. of sulphate of baryta was obtained, which gives 1·643 per cent. of nitrogen, or 6·3 per cent. of nitric acid, in the peroxide.

A second method is founded on the above-mentioned property of the peroxide, of giving off oxygen gas when heated to 230°, and changing into a mixture of oxide and nitrate of silver. By determining the quantity of the latter, the quantity of nitric acid contained in the peroxide could be immediately ascertained, as the nitrogen was now contained therein in the form of nitric acid. It was only necessary, after heating, to extract the nitrate by means of water, and to throw down the silver by muriatic acid. The precipitated chloride of silver was washed, dried, melted and weighed, the filter burnt, the ashes oxidized with nitric acid, mixed with muriatic acid, dried, heated and weighed. From 2·5097 grms. of peroxide, 0·4855 grm. of chloride of silver, or 7·2 per cent. of nitric acid, were obtained. The average of the nitrogen in the two investigations is 1·765 per cent., corresponding with 6·7 per cent. of nitric acid.

For the Determination of the Oxygen, which is united with silver to form the peroxide, the property possessed by the peroxide of transforming oxalic acid into carbonic acid was employed. The decomposition was performed in a small flask, furnished with a funnel-tube for introducing the acid, and connected with a small chloride of calcium tube, through which the carbonic acid gas was passed into a weighed Liebig's apparatus, and there absorbed by a solution of potash. After the termination of the decomposition and change of the peroxide into a white oxalate, atmospheric air was sucked through the apparatus for some time, and the carbonic acid then weighed. In this manner, 3·3101 grms. of peroxide gave 0·9117 grm. of carbonic acid; as 2 atoms of carbonic acid represent 1 atom of the oxygen of the peroxide, the quantity of this oxygen amounts to 5·008 per cent. Although this oxygen of the peroxide may be

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driven off at a temperature of 230°, it cannot be directly determined in this manner, because, as appeared on making the attempt, the water contained in the compound escaped at the same time; and the amount of the latter, owing to its smallness, could not be determined with accuracy.

Determination of the Water.—The peroxide, heated to 290° in a glass tube, lost 6·174 per cent. in weight. Deducting from this the quantity of oxygen calculated from the carbonic acid as above, =5·008, there remains for water 1·166 per cent.

Three *Determinations of the Silver* gave on the average 81·176 per cent. of that metal.

The entire amount of oxygen was estimated by calculation; a certain quantity of peroxide was dried in the air-bath at a temperature of 104°, and then left to cool over sulphuric acid. The peroxide, thus perfectly dried, was heated to redness, the per-centage residue of silver calculated, and this sum, together with the ascertained quantities of hydrogen and nitrogen, deducted from 100. The quantity of oxygen thus ascertained was 16·030 per cent.

According to this, the composition given below is obtained for the so-called peroxide of silver. Assuming that the nitrogen is contained in this substance in the form of nitric acid, the calculation leads to the formula $5AgO^2 + AgO\,NO^5 + HO$, as follows:—

Ag	81·176	6	81·097
O	16·030	16	16·023
N	1·765	1	1·753
HO	1·166	1	1·127

Such a combination of a peroxide with a salt is as yet without precedent, although several remarkable combinations of nitrates with other very different salts are known, as, for instance, the crystallizing combination of nitrate of potash with the double sulphuret of potassium and tungsten discovered by Berzelius, and the compounds described by Wöhler of nitrate of silver with cyanide of silver and cyanide of mercury, and of nitrate of potash with mellitate of potash.

Another mode of representing the constitution of this compound would be to suppose that it consists only of nitrate of peroxide of silver, composed according to the formula $(AgO^2)^6 + NO^5$, and that the water obtained is only mechanically included, in consequence of the rapid formation of the crystals; it would then contain in 100 parts—

Silver	81·19
Oxygen	17·05
Nitrogen	1·76

The quantity of nitric acid would then amount to 6·7 per cent., as indeed it was found to be on the average of the two examinations. A third mode of representing its constitution is to suppose that it might contain the so-called hyponitric acid, NO^4, and be a combination of this with peroxide of silver and water, according to the formula $6AgO^2 + NO^4 + HO$, which, as may be seen, contains the same elements in the same proportions as in the formula first proposed.

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Perhaps however this body is essentially peroxide of silver, which, owing to the rapid mode of formation of the crystals and the superposition of its particles, contains the nitrate and water only mechanically enclosed. It appears to be a circumstance in favour of this view, that, according to Fischer, the sulphate of silver furnishes a similar peroxide, which also contains sulphuric acid, and that, according to the author's observations, the fluoride of silver forms a similar black, but slightly crystalline substance, which in other respects behaves like the other peroxides, except that on being heated it evolves fumes which strongly corrode glass. Should such a mechanical admixture of the salts serving for its formation not be admitted, we must suppose that the peroxide of silver possesses the faculty of combining chemically with the most dissimilar salts of silver in definite proportions.—*Inaugural Diss., Göttingen*, 1852; *Chem. Pharm. Cent. Blatt.*, xxiii. 385.

Examination of Coffee Beans. By Prof. ROCHLEDER.

Schrader, long since, in the examination of coffee beans, made the observation, that the peculiar extractive matter of coffee, that is, a mixture of caffeotannic acid with caffeotannates and caffeine, yielded by dry distillation a crystalline substance, which, in its behaviour with salts of the peroxide of iron, exhibited a resemblance to the product of the dry distillation of the tannin of gall-nuts (pyrogallic acid). The author subjected pure caffeotannine, dried at 212°, to dry distillation. During the tumescence of the melting mass, there comes over at first water, then a thick liquid of a yellow colour and faint smell of carbolic acid, with which a few drops of a thick brown oil are mingled. There remains a large quantity of a porous charcoal in the vessel in which the distillation has been carried on. If the receiver be changed during the distillation, so as to keep the thick portion of the product separate, it soon solidifies into a white crystalline mass. This crystallized substance possesses all the properties of pyrocatechine.

The amount procured is very small; and taking into consideration the large quantity of residuary carbon and of the water formed, the decomposition which takes place in the dry distillation of caffeotannic acid may be represented by the following equation, as probably being nearest to the truth:—

2 equivs. of caffeotannic acid $= C^{28} H^{16} O^{14} = C^{12} H^6 O^4 + C^{16}$, pyrocatechine $+ 10$Aq.

Heat therefore effects a decomposition of the caffeotannic acid analogous to that which this acid undergoes when exposed to the air in the presence of an excess of alkali. The product which is formed under these circumstances also contains $C^{12} H^6$, but united with a different quantity of oxygen.

The formation of pyrocatechine from caffeotannic acid brings this acid into near connexion with catechine, which is found in a plant of the same natural family (*Uncaria Gambir*).

The decomposition of caffeotannic acid cannot be effected by

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dilute acids at the boiling-point of water. After boiling a watery solution of caffeotannic acid to which sulphuric acid had been added for eight hours, adding water from time to time to make up for the loss by evaporation, a small quantity of viridic acid had been formed by oxidation at the expense of the oxygen of the air, but the greatest part of the acid remained unchanged.

Caffeotannic acid yields a peculiar product of oxidation when it is exposed to the air in a solution containing bicarbonate of lime. The substance thus formed is always accompanied by viridic acid; but it is insoluble in water, especially if it contains a free acid, and of a violet-black colour; the lime compound is also deep violet.

Pfaff has stated, that the aqueous decoction of coffee beans is precipitated by a solution of sugar of lead, and that this precipitate, decomposed under water by sulphuretted hydrogen, yields a fluid, which, when evaporated to the consistence of a syrup, is separated by alcohol into a soluble portion, caffeotannic acid, and an insoluble part, caffeic acid.

The author repeated Pfaff's process with this variation, that the watery decoction of coffee beans was partially precipitated with sugar of lead. The first portions of the precipitate contained small quantities of an acid, which exhibited all the reactions of citric acid, but amounted at the highest computation to about 2 grs. in a pound of coffee beans. The later-produced portions of precipitate contained no more of this acid. The mass, thrown down by alcohol, dissolved in water, heated to the boiling-point, and added by degrees to a boiling solution of basic acetate of lead, gave a yellow precipitate, which, when washed with hot water and decomposed under water by sulphuretted hydrogen, gave a liquid which exhibited all the reactions of caffeotannic acid. When evaporated to the consistence of syrup and mixed with alcohol, some light flakes of an insoluble substance separated.

There are therefore not two acids, caffeotannic acid and caffeic acid, contained in coffee beans, but, except traces of citric acid, only caffeotannic acid. That a watery solution of the so-called caffeic acid of Pfaff becomes brown on exposure to the air arises from its containing alkali (caffeotannates of potash and soda become brown in the air, even on the addition of ammonia, not green).

That on heating it yields the odour of roasted coffee in a higher degree than the free acid is not to be wondered at, as other products of decomposition must be formed by dry distillation in the presence of bases than in their absence.

If the watery decoction of coffee beans be completely, instead of partially precipitated by solution of sugar of lead, this precipitate decomposed under water by sulphuretted hydrogen, and the resulting liquid evaporated to the consistence of a syrup, we shall find citric acid in the fluid, besides caffeotannic acid and caffeotannates. By the addition of alcohol, caffeotannic and citric acids are precipitated. If this precipitate be dissolved in water, a solution of sugar of lead throws down in it a white precipitate, which contains citric and acetic acids in combination with oxide of lead; the caffeotannic

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acid, or its lead salt, remains dissolved in the liquid containing acetic acid.

A lead salt thus prepared was long since examined by Liebig and Wöhler, and its analysis published in the Annalen der Chemie, vol. lxiii. p. 200. The composition of this salt was represented by the formula $5PbO + C^{12} H^5 O^{11} + C^4 H^3 O^3$. It was supposed at the time to be the lead salt of a peculiar acid, $C^{16} H^8 O^{14}$.—*Bericht d. Akad. der Wiss. zur Wien.*, Jan. 1852.

On the Preparation of pure Barium Compounds.

By Henry Wurtz.

The preparation of the compounds of barium in a state of absolute purity is a subject which has not generally received much attention from pharmaceutical chemists, in consequence of the hitherto limited application of these compounds, except in chemical analysis. The time however is undoubtedly close at hand when new developments in the arts will create a demand for pure barium compounds, as well as for very many other products now considered as pertaining exclusively to the laboratory. Indeed efforts have already been made to introduce the *chlorate of barytes* to the notice of pyrotechnists as a means of producing a green fire unequalled in beauty, and the pure carbonate has been for some time in use in England in the manufacture of superior varieties of plate and flint glass. The precipitated or purified native sulphate is also preferred as a water-colour pigment to white lead, being far more durable than the latter. I may here be permitted to mention a practical application of the carbonate, which has occurred to myself. I have found that sulphate of lime is totally precipitated from its solution by mixing therewith an equivalent quantity of the precipitated or finely-pulverized native carbonate of barytes, of course with the formation of sulphate of barytes and carbonate of lime. It is by no means improbable that this property may be made available in removing sulphate of lime from spring- or sea-water which is to be used in steam-boilers, thus preventing the formation of the troublesome incrustation which so often occurs, especially when it is considered that the sulphate of barytes which would be formed might easily be reconverted into carbonate, and used over again. Again, sulphate of lime might be removed in the same way from the brine in salt-works, thus contributing to the purity of the salt produced.

Recent improvements in chemical analysis have greatly increased the usefulness of barium compounds in the laboratory, especially of the carbonate, to which the late investigations of Prof. H. Rose and of Ebelmen have given a place in the very first rank among the reagents valuable to the chemist. Any suggestion therefore concerning the preparation of these compounds in a pure state cannot be considered as useless.

The sulphate of baryta is the only compound which occurs in sufficient abundance to be an œconomical source of the other barium compounds; and the enormous though illegitimate use of this sub-

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stance in the adulteration of white lead is so far fortunate as to render it an easy matter to obtain it in any required quantity already in a state of fine powder, which is so desirable in chemical operations.

The sulphate of baryta is always reduced to the state of sulphuret of barium, by exposing it to a red heat in intimate admixture with some carbonaceous substance, such as powdered charcoal, rosin, oil or flour. It is exceedingly difficult, however, if not impossible, to effect in this manner a complete decomposition of the sulphate. Indeed it is probable that in most cases the quantity of sulphuret obtained is not more than half that which is equivalent to the sulphate employed. A modification, which promises to be far more economical, was proposed by Dr. Wolcott Gibbs. His proposal was to submit the sulphate to the action of a current of common coal-gas at a red heat. It is evident that in this way a perfect decomposition may readily be accomplished, especially if the powdered sulphate is stirred during the operation, so as to expose fresh surfaces to the action of the gas.

The mass obtained after the reduction of the sulphate is submitted to the action of boiling water, and a solution obtained, which, according to Prof. H. Rose*, contains principally hydrate of baryta and hydrosulphate of sulphuret of barium, BaS, HS, formed by the reaction of equal equivalents of water and protosulphuret of barium. It almost invariably contains also a quantity of lime, probably in the form of hydrosulphate of sulphuret of calcium, or of hydrate of lime, proceeding from the almost constant concurrence of sulphate of lime with native sulphate of baryta. From the presence of this lime originates the principal difficulty in preparing pure barium compounds from this substance. Thus when the carbonate is prepared from the solution by precipitation with carbonate of soda or a current of carbonic acid gas, it is found contaminated with carbonate of lime, which is fatal to its use as a reagent in analysis. Also in examining many specimens of commercial *chloride of barium*, which is prepared from this solution by the addition of hydrochloric acid, boiling to separate hydrosulphuric acid gas which is evolved, filtration to separate the sulphur which is precipitated, and crystallization, I have always found it to contain a small quantity of chloride of calcium, which I have not been able to separate entirely by repeated recrystallizations. It has been proposed† to separate the chloride of calcium from chloride of barium by the use of very strong alcohol, in which the latter, when anhydrous, is insoluble. This method is rather expensive and troublesome, as it involves the evaporation to dryness of the chloride of barium solution, the reduction of the previously-ignited residue to a very fine powder, and digestion in strong alcohol. Attempts were made,—after some previous experiments, in which it was found that an aqueous solution of *oxalate of baryta* precipitated chloride of calcium, but not chloride of barium,—to separate the lime from a chloride of barium solution by addition of oxalate of baryta, or simply of a little oxalic acid; but it was soon found that oxalate of lime was

* Poggendorff's Annalen, lv. 416. † Gmelin's Handbuch, ii. 158.

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somewhat soluble in a solution of chloride of barium, so that a solution of oxalate of baryta gave no precipitate in a mixture of solutions of chloride of barium and chloride of calcium. It was found also that the precipitate formed by a little oxalic acid in a lime solution could be redissolved by addition of chloride of barium. It may also be mentioned, though irrelevant to the subject, that it was found that oxalate of lime was soluble in solutions of chloride of calcium, of ammonia, and of hydrochlorate of ammonia.

The well-known property of carbonate of baryta, which the recent investigations of Prof. H. Rose have rendered so important in the analysis of phosphates, of completely precipitating lime from its solution by a sufficiently long contact therewith, furnishes us however with a perfectly easy and cheap method of purifying the chloride of barium solution. In fact, a solution of chloride of barium to which chloride of calcium has been added having been treated with a little carbonate of baryta, and allowed to stand in contact with it for two days, with occasional agitation, was found on filtration to be free from lime. The only objection to this method is the considerable length of time required; but I must here describe an elegant modification, which was communicated to me by Dr. Wolcott Gibbs, and tested by him in his laboratory, that is, to add first to the solution of chloride of barium containing lime a little solution of hydrate of baryta, and then to pass through it a current of carbonic acid gas. The precipitate immediately formed contains of course all the lime.

The only impurity which is prevalent in commercial chloride of barium besides lime is, strangely enough, a trace of *lead*, which is almost always present, and sometimes in such quantity that the solution is immediately blackened by hydrosulphuric acid*. This is however very easily removed, either before or after the separation of the lime by the process of Dr. Gibbs, by passing a little hydrosulphuric acid gas into the solution, gently heating for a short time and filtering.

Commercial chloride of barium, thus purified, is probably the most convenient source of the other compounds of barium when required pure. Thus pure carbonate of baryta may be prepared from it by precipitation with carbonate of ammonia, or with carbonate of soda, which is free from silica, sulphuric acid and phosphoric acid.—*New York Journal of Pharmacy*, June 1852.

On a new Yellow Dyeing Agent for Silk and Woollen, discovered by M. Guinon *of Lyons. By* Robert Warington†.

In the early part of last year (March 2, 1851), a specimen of a material for dyeing silk of a fine clear yellow colour, without the aid of a mordant, was put into my hands for examination. It had

* It may be that leaden pans are used for the evaporation or crystallization of the commercial chloride of barium, which would sufficiently account for the presence of lead in the product.

† Communicated by the Author.

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been obtained in France, and was for the time supposed to be kept a secret. It was of the consistence of a soft extract, dissolved almost entirely in hot water, with the exception of a small quantity of brown resinous matter; and on the addition of a little tartaric acid, produced a fine clear yellow on silk by its being immersed in it for a short time; if a mordant be used, the colour is much faster. This substance proved, on chemical examination, to be the picric, nitropicric or carbazotic acid in an impure state.

As the parties for whom the investigation was undertaken wished to be informed as to a process for its manufacture, I made a series of experiments on this subject, and found that the action of nitric acid upon the resins of *Xanthorrhœa hastilis* and *X. arborea* afford an excellent product for this purpose. These gums are known in commerce, the first as gum-flavum, or yellow gum, and gum-acaroides, and that from the latter as black-boy gum, or grass-tree gum. The former was suggested some years since* by Dr. Stenhouse, as likely to prove the best source of carbazotic acid. As thus prepared, a very pure, dry, crystalline carbazotic acid is readily obtained, and at a very cheap rate, the resin yielding about half its weight of crude acid.

In October of last year I made application, through Dr. Playfair, to the Industrial Exhibition, to endeavour to obtain a small specimen of these gums, as exhibited in the Australian department, for the purpose of identification, and to ascertain their value, but unfortunately without success, having received a polite note from the Executive Committee, stating that my application would be taken into consideration when all public institutions had been supplied. Failing in this direction, I have since been able to ascertain that it can at present be obtained in the drug market in small quantities at from 36*s.* to 40*s.* the cwt.; and I have also learnt, that if there were a sufficient demand, it could be imported at from 14*s.* to 20*s.* the cwt., making the cost of carbazotic acid about 6*d.* the pound.

I may state that I also communicated this investigation and process to Professor Magnus of Berlin, during his sojourn in London in September 1851, and have since forwarded him a small parcel of the resin.

The process employed in France has since been published by M. J. Girardin of Rouen†, and consists in treating coal-tar with nitric acid. The price of the impure acid, as examined, is 25 francs the kilogramme, or about 9*s.* 6*d.* the pound avoirdupois.

On the Influence of the Salts of Iron on Vegetation.
By M. Lassaigne.

When salts of iron get access to soils which do not decompose them, and so, becoming dissolved, enter the plants, they act injuriously. They do no injury when they are decomposed by lime and siliceous compounds; the carbonate of the protoxide of iron is taken

* Memoirs and Proceedings of the Chemical Society, vol. iii. p. 10.
† Journal de Pharmacie et de Chemie, vol. xx., Jan. 1852.

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up without injury to the plants. A small addition of an iron salt causes no alteration in an ordinary soil; iron salts have no influence on the green colour of the leaves. The injurious effects of the salts of the protoxide of iron, and of the peroxide, consist in an adstriction which they exercise on the radicles; and if a small addition of iron to water with which plants are watered be of use, this does not depend on an absorption, but on an action on the tissues of the plant itself.

When iron salts have been found efficacious in destroying injurious plants, this effect depends on the radicles being pervious to the solution of iron; absorption causes the destruction of the plant. If salts, especially of the protoxide of iron, be added to soils the plants of which in their ordinary vegetation always contain a certain amount of iron, the amount of iron in their ashes is not raised above the usual normal and variable quantity which is generally contained in the ashes of the plants.—*Comptes Rendus*, xxxiv. p. 587.

On a new Compound of the highest Chloride of Sulphur with Sulphuric Acid. By H. Rose.

The author long since prepared the compound SCl^3+5SO^3, by treating chloride of sulphur with anhydrous sulphuric acid, and shortly afterwards Regnault succeeded in combining the chloride of sulphur, SCl^3, in another proportion with 2 atoms of sulphuric acid. Regnault, and most other chemists, regarded the compound procured by him as a sulphuric acid in which a third part of the oxygen is replaced by chlorine, a mode of representation moreover which had been extended to the combinations of chromic and other metallic acids with their corresponding chlorides, which are analogous in composition with the compound of sulphuric acid and perchloride of sulphur.

The author had previously observed on this subject, that the highest chloride of sulphur, SCl^3, also united in more than two proportions with sulphuric acid, and that these compounds are contained in those crystallized products obtained by the distillation of a solution of an excess of anhydrous sulphuric acid in chloride of sulphur, but that it is very difficult to separate them from the excess of sulphuric acid, and from the sulphate of perchloride of sulphur, SCl^3+5SO^3.

The author, many years ago, saturated chloride of sulphur with chlorine gas, and allowed it to absorb a great excess of anhydrous sulphuric acid, until at last a portion of the acid separated itself from the solution in a crystalline form. The flask was then hermetically closed. After some time the fluid portion had also completely changed into white silky crystals, which remained unchanged for several years even during the hot summer months. The flask was kept seventeen years. In the course of this time, a small quantity of fluid had formed at the bottom; but from the glass stopper with which the flask was closed, almost to the bottom, it was filled with radiating crystals, which externally resembled the

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crystallization of some kinds of zeolites, especially that of mesotype. On opening the flask, the compound emitted copious fumes like anhydrous sulphuric acid, and like this it exploded when thrown into water; the solution contained sulphuric and muriatic acids. On analysis it was found to consist of 31 atoms of sulphur, 3 equivs. of chlorine and 90 atoms of oxygen, so that its composition may be expressed by the formula $SCl^3 + 30SO^3$.

Thus we are acquainted at present with the three following compounds of the highest chloride of sulphur with sulphuric acid:—

1. $SCl^3 + 2SO^3$.
2. $SCl^3 + 5SO^3$.
3. $SCl^3 + 30SO^3$.

Bericht der Acad. der Wissensch. zu Berlin, 1852, p. 167.

On the Crystallizability of one of the principal Constituents of the Blood-Corpuscles. *By* Prof. Lehmann.

The author has been long endeavouring to effect the crystallization of the albuminous substances. The results of these investigations have not turned out unprofitable, and the author here communicates those which he has procured, in conjunction with some of his pupils, in operating upon blood. Dr. Funke, whilst engaged in the examination of the blood of the spleen of the horse, first made the discovery, that this blood, by gradually drying between the object-plates during microscopic observations, changed almost completely into prismatic crystals; and it was afterwards found that the whole of the blood of many freshwater fishes was capable of crystallization. Funke has published his observations in Henle and Pfeiffer's 'Zeitschrift für Rat. Med.' The author ascertained that the blood of the portal vein of the horse furnished prismatic crystals exactly similar to those of the blood of the spleen. Dr. Zenker of Dresden found, that in a case of leucæmia with enormous enlargement of the spleen, the entire blood crystallized in exactly the same manner as the blood of the spleen in other cases. D. Kunde of Berlin also saw the blood of dogs, both in health and diseased, form prismatic crystals.

The discovery of Reichert, according to which tetrahedral proteine crystals occur on the decidua of a pregnant guinea-pig, led the author to think that these crystals might be nearly allied to the blood crystals; and, in fact, he found these tetrahedral crystals on the decidua of such an animal, as Kunde had also found them in the common blood of the guinea-pig. No other crystals but these tetrahedra of the blood existed in the decidua. The author also found that the blood of the mouse, and Kunde that of the rat, crystallized in tetrahedra. The latter however discovered the most elegant crystallization in the blood of the squirrel, which furnished most beautiful large six-sided prisms (not belonging to the hexagonal system); sometimes there appeared also well-formed, six-sided columns, truncated at right angles.

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It was probable that the blood of the portal vein and that of the spleen of these animals crystallized in prisms; but it was found that the blood of the portal vein at least always furnished crystals of the same form as those of the rest of the blood; it is however generally less inclined to crystallization than the blood of the other veins. Well-oxygenated blood, or blood artificially impregnated with oxygen, generally crystallizes more readily than that which is rich in carbonic acid. The blood of birds could not be made to crystallize in spite of variously-modified experiments, and the same was the case with human blood, the blood of the horse, ox, &c.

However interesting these observations may appear in themselves, there was really not much gained by them, as this crystallization could only be produced between glass-plates. It was easy to see, that for the production of these crystals an extremely gradual evaporation was to be contrived. The author consequently constructed various apparatus, by which the progress of the evaporation was brought tolerably under command; the destruction of the blood-corpuscles is however an essential means of advancing the crystallization, for that their contents furnished the crystals had already been easily ascertained by microscopic observation (the serum never crystallizes, even when it contains a large number of blood-corpuscles). Moreover, if the blood-corpuscles do not require to be completely destroyed, it was necessary, nevertheless, for the production of the crystals, to contrive a rapid endosmosis between their contents and the surrounding fluid. The latter is effected by means of water, or better by æther or alcohol, but best of all by water and æther. Blood thus mixed was put into a cylindrical apparatus, closed at one end with pig's bladder, at the other with a sheet of india rubber; weak spirit was made to pass through the caoutchouc until the blood began to grow turbid; the apparatus was then exposed to a temperature of from 59° to 68°, when water evaporated through the bladder, spirit through the india rubber, and the most beautiful crystals were formed (in the blood of the guinea-pig as much as $\frac{3}{4}$ line in diameter). However, it is often only necessary to have a piece of india rubber tube, closed at one end with bladder, and furnished at the other with a cork, which is pierced by a capillary tube, so that the pressure of the air may not prevent the evaporation through the bladder. Moreover, blood-clot, or the sediment of blood-corpuscles washed with water, gives the best crystals.

The tetrahedral crystals of the blood of the guinea-pig are very difficult of solution in water; but in spite of this, the purification of the crystallizable matter presents many difficulties. The following method has hitherto been found the best:—The collected crystals are repeatedly agitated with water, by which a great part of the envelopes of the blood-corpuscles, and other particles separated with the crystals, are removed; but the sticky envelopes of the corpuscles not only cling to the crystals, but are frequently enclosed in them; the crystals are therefore to be dissolved in water at 104°–122°, and filtered; even a tolerably concentrated solution of the blood-corpuscles may be readily filtered in this manner, and freed from the

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envelopes. The recrystallization however does not take place so readily as one would have expected; this may be partly owing to the absence of the envelopes of the blood-corpuscles, which serve as points of support for the crystallization.

The crystals contain a very large quantity of hydrate-water, and effloresce very rapidly in the atmosphere; they however do not become powdery and opake, but split, and then form irregular horn-like pieces with a shelly fracture. Their solution is curdled at 144°–156°, not by acetic acid, but by alcohol, mineral acids, and all the other agents by which proteine substances are usually precipitated. The crystals consist of albuminous matter and mineral substance, analogous to the well-known combination of diabetic sugar and common salt.—*Journ. für Prakt. Chem.*, lv. 65.

Investigation of the Leaves of Rubia tinctorum.
By Erwin Willigk.

On the recommendation of Prof. Rochleder, and in connexion with his observations on the family *Rubiaceæ*, the author has examined the herb of *Rubia tinctorum*. He found, with small quantities of lime, magnesia and phosphoric acid, sulphuric acid, a tannic acid producing a green colour with iron, citric acid and rubichloric acid.

Tannic Acid (Rubitannic Acid).—A portion of the dry herb was exhausted with boiling water, the filtered liquid precipitated with acetate of lead, the precipitate digested with dilute acetic acid, and the insoluble part filtered from the liquid.

The salt dissolved in the acetic acid was precipitated with ammonia, the precipitate washed with alcohol, decomposed in alcohol of 0·83 by sulphuretted hydrogen, the liquid filtered from the sulphuret of lead, mixed with a large quantity of water after the alcohol was expelled, and precipitated with basic acetate of oxide of lead; the precipitate was again decomposed under water by sulphuretted hydrogen, the liquid filtered from the sulphuret, and evaporated in the water-bath. The liquid gave a fine green colour with perchloride of iron, and a reddish-brown colour with ammonia. The acid was dried *in vacuo*; it was very hygroscopic.

Prepared in this manner, the acid still contains small quantities of lime and magnesia. Analysis gave the following results, after deducting the incombustible residue:—

Carbon	43·00	28	= 168	42·96
Hydrogen	5·89	23	23	5·88
Oxygen	51·11	25	200	51·16

From this the formula is $C^{28} H^{23} O^{25} = 2(C^{14} H^{11} O^{12}) + HO$, or in unison with the lead salts mentioned below, $2(C^{14} H^{8} O^{9}) + 7HO$.

A lead salt of the tannic acid was obtained in the following manner:—A portion of the fresh herb was exhausted with boiling water, the filtered liquid precipitated with acetate of lead, the brown precipitate collected and washed with water, and then digested with

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dilute acetic acid. The solution in acetic acid, filtered from the insoluble residue, was precipitated by ammonia, the precipitate filtered from the liquid, washed with water, and decomposed with sulphuretted hydrogen; the liquid filtered from the sulphuret of lead, after the excess of sulphuretted hydrogen had been driven off, was precipitated by basic acetate of lead, and the yellowish precipitate washed with water and dried at 212°. The analysis of the salt gave the following result:—

Carbon.....	11·50	70 =	420·00	11·71
Hydrogen	1·42	50	50·00	1·39
Oxygen	12·34	55	440·00	12·26
PbO.....	74·74	24	2677·44	74·64

A simple formula, which also agrees very closely with the results of the analysis, is $C^{14}H^{10}O^{11}, 5PbO = C^{14}H^{8}O^{9}, 3PbO + 2(PbO, HO)$.

A second lead salt was prepared in the following manner:—A portion of the fresh herb was exhausted with boiling water, the filtered liquid precipitated by acetate of lead, the precipitate collected on a filter, washed out with water, and then digested with dilute acetic acid. The solution in acetic acid was precipitated with basic acetate of lead, the resulting precipitate washed with water, and decomposed under water by sulphuretted hydrogen; the liquid filtered from the sulphuret of lead, after the excess of sulphuretted hydrogen had been driven off, was precipitated with acetate of lead, and the yellow precipitate dried *in vacuo*. The analysis of this gave the following result:—

Carbon.....	19·97	56 =	336·00	20·13
Hydrogen	2·19	33	33·00	1·98
Oxygen	17·79	37	296·00	17·73
Oxide of lead	60·05	9	1004·04	60·16

$C^{56}H^{93}O^{37} + 9PbO = 4(C^{14}H^{8}O^{9}, 2PbO) + (PbO, HO)$.

A third lead salt was obtained by exhausting a portion of the dried herb with boiling water, and mixing acetate of lead with the filtered liquid until a sample of the precipitate was completely soluble in acetic acid; the liquid was then filtered from the resulting precipitate, and completely precipitated. The precipitate was collected on a filter, washed with water, and afterwards mixed with water, and decomposed with sulphuretted hydrogen.

The liquid filtered from the sulphuret of lead, after the excess of sulphuretted hydrogen had been expelled, was precipitated with acetate of lead. The yellow precipitate, dried at 212°, gave the following numbers on analysis:—

Carbon.....	14·74	28 =	168·00	14·79
Hydrogen	1·63	19	19·00	1·67
Oxygen	14·97	21	168·00	14·79
Oxide of lead	68·66	7	780·92	68·75

$C^{28}H^{19}O^{21} + 7PbO = 2(C^{14}H^{8}O^{9}, 2PbO) + 3(PbO, HO)$.

Citric Acid.—The presence of citric acid was shown in the following manner:—The decoction of the fresh plant was precipitated

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with acetate of lead, the liquid portion filtered and mixed with basic acetate of lead, the resulting precipitate collected on a filter, washed with water, and then decomposed under water by sulphuretted hydrogen; the liquid filtered from the sulphuret of lead was then precipitated with acetate of lead, and the precipitate digested in dilute acetic acid, in order to remove the last traces of tannic acid. The portion dissolved in acetic acid was filtered from the insoluble residue, the latter washed with water, and decomposed under water by sulphuretted hydrogen. The liquid filtered from the sulphuret of lead was concentrated in the water-bath, and then placed under the bell of the air-pump.

After some time, crystals were deposited in the syrupy fluid, which had exactly the appearance of crystallized citric acid. The entire mass was mixed with alcohol of spec. grav. 0·803, filtered from the small insoluble residue, and precipitated whilst hot with an alcoholic solution of sugar of lead. The precipitate was washed with alcohol and dried at 212°. On analysis it gave the following numbers:—

Carbon	16·96	48	= 288·00	16·94
Hydrogen	1·45	24	24·00	1·41
Oxygen	22·51	48	384·00	22·59
PbO	59·08	9	1004·04	59·06

$$C^{48}H^{24}O^{48}+9PbO=4(C^{12}H^{5}O^{11}+HO)+9PbO.$$

On deduction of the oxide of lead:—

Carbon	41·45	12	= 72	41·38
Hydrogen	3·54	6	6	3·45
Oxygen	55·01	12	96	55·17

This mode of preparation, by which citrate of lead only is always procured, is that given by Heldt, whilst by other processes a double citrate and acetate of lead is obtained.

Rubichloric Acid.—Rubichloric acid is contained, together with citric acid, in the precipitate produced by basic acetate of lead in a decoction of the madder plant which has been precipitated by neutral acetate of lead, but in larger quantity in the liquid filtered from this precipitate.

A lead salt of this acid was formed in the following manner:—After the decoction of the herb had been precipitated by acetate of lead and filtered from the resulting precipitate, it was precipitated by basic acetate of lead, the precipitate collected on a filter, washed with water, and decomposed under water by sulphuretted hydrogen, the liquid filtered from the sulphuret of lead, and after the excess of sulphuretted hydrogen had been driven off, again precipitated with acetate of lead; the precipitate of citrate of lead was separated, and the filtered clear liquid mixed with strong alcohol to remove the last traces of citric acid, by which a white precipitate was produced, which was also separated.

The alcoholic liquid filtered from this precipitate was mixed with a large quantity of water, and precipitated with basic acetate of lead, the precipitate washed with water, and then decomposed by sulphu-

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retted hydrogen; the liquid filtered from the sulphuret of lead did not produce a green colour with perchloride of iron; boiled in muriatic acid, it deposited a plentiful precipitate of a green colour. The liquid was precipitated by basic acetate of lead, the yellow precipitate collected on a filter, washed with water, and dried at 212°. The analysis of this salt gave the following result:—

Carbon	8·56	28	= 168·00	8·60
Hydrogen	1·19	23	23·00	1·18
Oxygen	10·21	25	200·00	10·24
PbO.....	80·04	14	1561·84	79·98

$C^{28} H^{23} O^{25}, 14PbO = (C^{14} H^{8} O^{9}, 3PbO) + (C^{14} H^{8} O^{9}, 4PbO) + 7(PbO, HO)$.

A second lead salt was obtained in the following manner:—The decoction of the plant was precipitated with basic acetate of lead, the liquid filtered from it mixed with a few drops of ammonia, strongly evaporated, and then completely precipitated by ammonia. The precipitate was digested in hot alcohol to render it pulverulent, washed with alcohol, as when washed with water it becomes very gelatinous and stops up the pores of the filter, and decomposed under water by sulphuretted hydrogen. The liquid filtered from the sulphuret of lead, after the excess of sulphuretted hydrogen had been driven off, was decomposed by acetate of lead; and as no precipitate was produced, mixed with warm alcohol; the resulting yellowish-gray precipitate was washed with warm alcohol, and dried at 212°. It gave on analysis the following numbers:—

Carbon	16·85	140	= 840·00	16·95
Hydrogen	1·92	90	90·00	1·82
Oxygen	16·30	100	800·00	16·14
PbO	64·93	29	3225·24	65·09

$C^{140} H^{90} O^{100}, 29PbO = 10(C^{14} H^{8} O^{9} + HO) + 29PbO$; on deduction of the oxide of lead, $C^{14} H^{9} O^{10} = C^{14} H^{8} O^{9} + HO$.

If a solution of rubichloric acid be heated with muriatic acid, a green powder, soluble in alkalies with a red colour, is deposited; it is chlorrubine, which has already been analysed by Rochleder and Schwartz.

Boiled with nitric acid and strongly evaporated, beautiful, distinctly formed crystals of oxalic acid are separated after some time from the solution of rubichloric acid.

On analysis of the ashes of *Rubia tinctorum* a considerable quantity of sulphuric acid was found.—*Bericht der Akad. der Wissensch. zu Wien*, Jan. 1852.

Method of Crystallization by means of an uninterrupted Circulation. By M. Payen.

To procure substances in larger and more regular crystals than is possible by the ordinary processes, the author has made use of a

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very simple apparatus, in which a constant current is produced by a slight difference of temperature. An alembic is furnished at the top with a head, and both are filled with the substance to be dissolved. From the head a tube enters the top of a vessel standing beside it. A second tube goes from the base of this vessel into the alembic. All these vessels, alembic, head and supplementary vessel, together with the tubes, are filled with the solvent, and by heating the alembic on the water-bath by means of a spirit-lamp, a constant current is produced, in consequence of which, crystals, which gradually increase in size, are formed in the supplementary vessel. By treating sulphur and benzine in this manner, the author obtained octahedral crystals of sulphur of much larger size than by any other method.—*Comptes Rendus*, xxxiv. p. 578.

Analysis of a new Alloy for the Plates for Calico-Printers. By Conrad Fischer.

A white alloy, which is peculiarly adapted for the plates used in calico-printing, and is used for that purpose in Ghent, has the following composition:—

Tin	46·81
Lead	37·44
Bismuth	15·75

Journ. für Prakt. Chem., lv. p. 192.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

June 7th, 1852. (Colonel Philip Yorke, Vice-President, in the Chair.) The following papers were read:—

"Note on the Existence of Strontia in the Well-Waters of Bristol," by William and Thornton J. Herapath.

The attention of the authors was first directed to this subject in consequence of the discovery of a small quantity of sulphate of strontia in the deposit found in a water-pipe. On carefully examining the well-waters from different parts of the city and its suburbs, sulphate of strontia was found, to a greater or less extent, in most of them. The method adopted for the detection of this ingredient was, to evaporate the water to dryness; to treat the residue with pure sulphuric acid, driving off the excess of acid by heat; then to treat first with boiling water, and subsequently with hot hydrochloric acid, until everything soluble in these menstrua was removed, leaving the sulphate of strontia together with silica. In order to separate these two substances, they were exposed in a platinum crucible to the vapour of hydrofluoric acid, by which means the silica was abstracted and the sulphate of strontia left.

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"On a new Method for the Analysis of Chrome Ores, and on Commercial Chlorochromate of Soda," by F. C. Calvert.

For the method usually adopted for the analysis of chrome ores, the author proposes to substitute the following:—The ore, well pulverized, is mixed with about three or four times its weight of a mixture made by slaking quick-lime with caustic soda, and then drying and calcining the mass. To these about one-fourth part of nitrate of soda is added, and the mixture is calcined for about two hours. By this method one treatment is generally sufficient to convert the chromium into chromic acid, whereas by the usual method five or six successive calcinations are required.

Another process, which he has also found to produce good results, consists in calcining the pulverized chrome ore with nitrate of baryta, adding a little caustic potash from time to time towards the end of the process.

Commercial chlorochromate of soda was found by analysis to contain chromic acid, chlorine, sulphuric acid, potash and soda. The author assigns to it the following composition:—

Bichromate of potash	23·16
Chlorochromate of soda	17·33
Chloride of sodium.....	33·71
Sulphate of soda.....	25·66
Insoluble matter.....	0·21

"On certain Isomeric Transformations of Fats," by Patrick Duffy.

A great number of observations are recorded in this paper, showing that stearine and some other fats may be obtained in different allotropic conditions in which they have different melting-points.

"On the Qualitative Separation of Arsenic, Tin and Antimony," by George F. Ansell.

The method proposed by the author consists in dissolving the mixed sulphurets in nitrohydrochloric acid, and pouring the solution into an apparatus in which hydrogen gas is generated in the usual way. The evolved gases are first passed through a wash-bottle containing solution of acetate of lead, to remove any hydrochloric acid or sulphuretted hydrogen, and are then conveyed into a test-tube half-filled with strong nitric acid. The nitric acid solution obtained after the gases have passed for about a quarter of an hour is evaporated to dryness, and the residue, which will contain the arsenic originally present partly in the state of arsenic and partly of arsenious acid, and the antimony in the state of antimonic acid, is exhausted with warm water, which takes up the first two and leaves the last-named substances. The tin remains in the vessel in which the hydrogen was generated. These are severally identified by the application of the appropriate tests.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Presence of Iodine in various Plants, with some Remarks on its general Distribution. By STEVENSON MACADAM, Esq.

THE present paper owes its origin to some observations lately made by M. Chatin of Paris, and communicated by him to the French Academy of Sciences.

Chatin is of opinion, that in the atmosphere, in rain-water, and in soils there is an appreciable amount of iodine; that the quantity of this element present in one district differs from that in another; and that the relative amount of iodine in any one locality determines to a great extent the presence or absence of certain diseases. For instance, in the district of country which he classifies under the general title of the "Paris zone," the quantity of iodine present in the atmosphere, in the rain-water, and in the soil is comparatively great, and to this he ascribes the absence of goitre and cretinism; whereas in the zone corresponding to that of the "alpine valleys," the amount of iodine has diminished to one-tenth of that found in the "Paris zone," and to this scarcity of the element he attributes the prevalence of goitre and cretinism, which in that zone are endemic. Considering that the subject was one of great importance, more especially if the conclusions arrived at by Chatin (in reference to the functions fulfilled by iodine in preventing the occurrence of the diseases referred to) could be legitimately deduced from the experiments which he performed, the author has this summer undertaken a series of analyses in reference to the general distribution of iodine. Mr. Macadam's researches have as yet been mostly directed to the atmosphere and to rain-water, and he considered that a notice of the results obtained might be interesting to the Society, alike from the intimate connexion which exists between the plant and the atmosphere, and from the fact, that he has been led to seek, and to detect, the presence of iodine in a department of the vegetable kingdom in which it has not hitherto been observed.

Chatin has not published a detailed account of the processes adopted by him; but from the manner in which he speaks of the good effects produced by the addition of potash to substances under examination, which, to use his words, "arrested the complete decomposition of the iodine compounds whilst the waters were evaporating," and by the addition of carbonate of potash and carbonate of soda, which "rendered the iodine present in soils much more easily extracted," the

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author was led to believe that the fixed alkalies had been largely employed by him. Accordingly, in the first experiments, the alkalies were used in their caustic condition, for the purpose of fixing any free iodine, and retaining any compound of iodine which might be encountered.

Mr. Macadam commenced with an examination of the atmosphere. By the arrangement he employed, the air was made to traverse,—1st, a tube containing slips of paper, which had been previously dipped in a solution of starch; and 2nd, a double-necked gas bottle, containing about 3 oz. of a dilute solution of caustic soda. A continuous stream of air was drawn through the arrangement for some hours. This experiment was conducted in the morning, and in the afternoon a stream of air was for several hours drawn through the same arrangement, caustic potash being substituted for the caustic soda. The starch-papers did not exhibit the slightest coloration, even when moistened with distilled water. The solutions of potash and soda, however, on being treated with starch and nitric acid, at once exhibited the rose colour characteristic of the presence of iodine in small quantity. So far the experiments seemed to lead to the desired conclusion; but when portions of the original alkaline solutions, which had not been subjected to a current of air, were carefully tested, it was found that iodine was present in them, in quantity to all appearance as great as it was in those portions which had been used in the experiments.

Wishing to trace back the iodine to its source, samples of the carbonate of potash, carbonate of soda and lime, which had been employed in the preparation of the caustic solutions, were analysed, and in all three iodine was present in perceptible quantity. Desirous of making certain that the reagents used in the investigations were as pure as other commercial substances of the same kind, various specimens were procured from different sources, and in every sample which was subjected to examination the presence of iodine was detected. So far then as the determination of iodine in the atmosphere is concerned, the experiments were of no value. The alkalies through which the air had been drawn undoubtedly contained iodine originally, and therefore no certain conclusion could be drawn as to the probability of their being more highly iodized by contact with the atmosphere. To the presence of iodine in *potashes*, or, to use words more strictly botanical, in the *ashes of forest timber*, further reference will be made in a subsequent part of this paper.

In the next experiment the alkalies were dispensed with, the air being drawn through—

1. A tube with slips of starched paper, kept somewhat damp.
2. A gas-bottle immersed in a freezing mixture; and
3. A gas-bottle containing a solution of nitrate of silver.

A continuous current was kept up for fully five hours, commencing at mid-day. At the conclusion of this experiment, the papers were not altered in the slightest degree; the gas-bottle (2) contained about a quarter of an ounce of liquid, and the nitrate of silver (3) had not been perceptibly changed. The condensed liquid was neutral to test-

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papers; a drop of starch was added to it, and subsequently nitrite of potash and hydrochloric acid, which together form a most delicate means of detecting iodine; the result was negative. The nitrate of silver solution was cautiously evaporated to one-half ounce; sulphuretted hydrogen added to precipitate the silver, and liberate as hydriodic acid any iodine which might be present; the liquid raised in temperature, carefully avoiding ebullition, and filtered. The filtrate, on the addition of starch, nitrite of potash and hydrochloric acid, did not exhibit the slightest trace of iodine. Mr. Macadam therefore concluded, that in the large volume of air which he had drawn through the arrangement, there had not been an appreciable amount of iodine.

The experiments as yet referred to were made at different heights on Arthur's Seat, and their negative results led to arrangements being made for a trial on a scale much more extensive. Through the kindness of the proprietor of Kinneil Iron Works, the author was enabled to proceed to Borrowstowness, and attach his apparatus to the receiver from which the air under great pressure is forced into the blast-furnaces. By means of a stop-cock fixed in the receiver and a long flexible tube, the air was conducted to the following arrangement:—

1. A wide tube containing slips of paper dipped in starch.
2. A condensing worm, surrounded by a freezing mixture and attached to a receiver.
3. A tall jar containing chips of pumice-stone and a few iron filings, with sufficient water to cover them.
4. A similar jar with pumice-stone, scrapings of clean lead and a solution of acetate of lead.
5. A condensing worm immersed in a freezing mixture and attached to a receiver.

The air, under a pressure of 3 lbs. on the square inch, was allowed to traverse the arrangement for fully four hours, when the apparatus was taken asunder, and the contents of the vessels being placed in stoppered bottles, the whole was brought to Edinburgh for examination. The slips of paper (1) were not sensibly altered in tint, and did not betray the slightest indications of even a rose colour when moistened with distilled water. The condensers (2 and 5) contained each a very small quantity of liquid, which, on being tested, did not show a trace of iodine. The small quantity of liquid in the condensers may be accounted for by the comparatively high temperature possessed by the air rushing through so quickly as it did. The contents of the jar (3) were thrown on a filter, and washed with cold water. To the filtrate was added half an ounce of a solution of carbonate of potash, and the whole evaporated to a quarter of an ounce; no iodine was present. The carbonate of potash used in this trial was prepared by calcining cream of tartar, and was so far free from iodine, that none could be detected in 2 oz. of the solution, of which half an ounce was employed. There was therefore no likelihood of iodine being added in the alkali used, even though the analysis of the contents of the jar had shown its presence. The jar (4) with the lead solution was treated in the same manner as described in a former

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part of this paper, when referring to the employment of silver, and the result was also negative. Notwithstanding the large scale on which this experiment was conducted, a volume of air of not less than 4000 cubic feet having been forced through the arrangement, Mr. Macadam has been unable to verify the results of Chatin, yet he feels disinclined to pronounce those results unwarranted, and has therefore resolved to make another trial on a still larger scale. It is proposed to fit up an apparatus of a stronger and more durable nature, and to allow a volume of air of not less than 100,000 cubic feet to pass through.

Whilst the experiments on the atmosphere were proceeding, Mr. Macadam was also examining large quantities of the rain-water which fell in Edinburgh for the last two months. For this purpose, he added to 3 gallons of the water some ounces of a solution of acetate of lead. On standing twenty-four hours, a precipitate had fallen to the bottom, from which the liquid was drawn off. The precipitate was treated as formerly described, and no iodine was detected. As the iodide of lead is slightly soluble in water, and as it might be present in the liquid which had been removed from the precipitate, the whole was evaporated to 1 oz., and afterwards tested for iodine, but none was present. A second experiment was tried with a similar volume of rain-water, viz. 3 gallons, substituting nitrate of silver for the acetate of lead; a precipitate was observed after standing for twenty-four hours, but neither it nor the liquid contained a trace of iodine. Another experiment, made with 3 gallons of rain-water, which had been collected at Unst in the Shetlands, and to which acetate of lead was added, gave the same negative results.

Mr. Macadam is well aware, that, consequent on the evaporation of water from the surface of the ocean, portions of the salts contained in it are carried up and disseminated through the atmosphere, ready to be rained down upon inland places, and that in this way iodine, most probably as iodide of sodium, will be present in the air. Accordingly at first he was confident that he should succeed in verifying Chatin's observations in a district so near the sea as that around Edinburgh, and more especially in the water obtained from Unst, which had fallen in the immediate vicinity of the ocean; but when we consider what a very small per-centage of iodine is present in the water of the ocean, many gallons being required to give even a faint indication, equal to that exhibited by $\frac{1}{500,000}$th of a grain of an alkaline iodide, and if, further, we suppose that when the water rises in vapour from the sea, it carries up the salts in the same proportions as they exist in sea-water, it is evident that it would be requisite to evaporate some hundred gallons of rain-water, before even a minute trace of iodine could be obtained.

At a former part of this paper reference was made to the presence of iodine in the potashes of commerce. The samples first tested were those usually to be purchased in Edinburgh, but subsequently genuine and authenticated specimens of both crude and refined potashes were procured from Glasgow. It is to Canada and the United States that we owe our supplies of these materials. As imported into this country,

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they are contaminated with many foreign ingredients, and amongst the rest the author has detected iodine. The most ready means for separating and recognising this substance is to heat a considerable quantity of the salt with a minimum of water. On cooling the solution, the greater portion of the carbonate of potash, as well as the impurities, falls to the bottom of the vessel, whilst the iodide of potassium remains dissolved in the water. When testing for the iodine in the potashes, this solution was evaporated to dryness, treated with alcohol, boiled and filtered. The filtrate, on being evaporated to dryness, left a residue, which on resolution in water acted distinctly with the starch-test for iodine.

The presence of this element in potashes leads the author to believe that iodine will be found more generally distributed in the vegetable kingdom than it has formerly been supposed to be. The potashes from the States and from Canada are principally the dried lixivium of the ashes of forest-trees; but whilst by much the greater portion is so, the parties in charge are not very scrupulous about what plants they employ, and occasionally everything which comes in the way, and which will burn, is added to the pile. It may therefore be objected to the statement, that forest-trees contain iodine, that the iodine found in the ashes may be derived from the succulent herbs and shrubs, and not from the trees themselves; but this objection will be at once removed when it is stated, that in the lixivium of charcoal the author has obtained very distinct traces of iodine. Now the charcoal sold and used in this country is principally oak, with a little birch, elm and ash.

The amount of iodine in forest-trees must be comparatively small. When experimenting with the potashes, one is apt to forget the small bulk into which a large quantity of timber falls when the organic matter is expelled, and the saline ingredients are alone left. So far as can be estimated from the present qualitative experiments, the relative quantity of iodine in forest-trees is much less than that in succulent plants growing in marshy places.

In conclusion, it was mentioned that the presence of iodine in some freshwater plants was now generally recognised, and that the author is at present engaged in testing the various plants growing in the lochs in the neighbourhood of Edinburgh. The method employed in their analysis is to dry the plants, and burn them cautiously; indeed the *burning* should be rather termed *charring*; the ashes are reduced to fine powder, digested in water and filtered; the clear liquid evaporated, and subsequently treated like the potashes. In every case the process used for the liberation of iodine is that suggested by Dr. Price*, viz. nitrite of potash and hydrochloric acid; and in many cases where no indications of iodine could be obtained by the ordinary methods, good results were procured with Dr. Price's process.

In the following plants, hitherto not known to contain iodine, Mr. Macadam has detected that element:—

Myosotis palustris..... Duddingstone Loch.
Mentha sativa ..... Ditto.

* Chem. Gaz., vol. ix. p. 293.

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Menyanthes trifoliata	Duddingstone Loch.
Equisetum limosum	Ditto.
Ranunculus aquatilis.....	Dunsappie Loch.
Potamogeton densus	Ditto.
Chara vulgaris	Ditto.

The author has also confirmed the presence of iodine in the following plants, in which it had been previously found by other observers; the specimens, however, are from different localities:—

Iris pseud-acorus	Duddingstone.
Phragmites communis	Ditto.

And in the ashes of coal.

As having some connexion with the subject treated of, the author intimated that he had obtained distinct indications of the presence of bromine in the crude potashes. It is unfortunate that our tests for bromine are so much inferior in delicacy to those of iodine, that it is necessary to operate upon very large quantities before the tests are distinct. There is no doubt that from its presence in trees, it will be found in greater abundance in the more succulent plants; but the few trials yet made have been unsuccessful in determining its presence in any but the crude Canadian and American potashes.

The experiments (excepting those pursued in the open air) were conducted in the laboratory of Dr. George Wilson, to whom the author feels deeply indebted for the kind manner in which he has afforded him every assistance in his power during the whole course of the investigation.—*Proceedings of the Botanical Society of Edinburgh*, July 8, 1852.

Chemical Examination of the Rubiaceæ. *By* F. Rochleder.

The author has devoted himself for several years to the examination of a single family of plants. The results of these investigations have confirmed the fact already frequently stated, that the same or similar substances are very often produced in allied plants, and undergo similar transformations in their œconomy. He has now put together the following general results of his experiments upon some of the most interesting plants of the family *Rubiaceæ*.

1. The beans of *Coffea arabica* contain, besides some sugar, fatty matter and legumine, caffeotannic, viridic and citric acids and caffeine.

2. In the root of *Cephaëlis ipecacuanha* there are ipecacuanhic and pectic acids, gum, starch, and some fatty matter and emetine.

3. In the root of *Chiococca racemosa*, caffeotannic and caincic acids and emetine (?) are met with.

4. In the bark of *Portlandia grandiflora* (*China nova Xauxa*), chinovatannic acid, chinova-red, gum, kinic and kinovic acids are contained.

5. The bark of *Cinchona scrobiculata* contains cinchonatannic acid, cinchona-red, kinic acid, kinovic acid, cinchonine, cinchotine and quinine.

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6. The herb of *Asperula odorata* contains aspertannic, rubichloric and citric acids, coumarine and catechine.

7. The herb of *Rubia tinctorum* contains rubitannic, citric and rubichloric acids.

8. In the root of *Rubia tinctorum* there are present rubichloric, citric, ruberythric and pectic acids, alizarine, purpurine and sugar.

9. In the herb of *Galium verum*, galitannic, rubichloric, and citric acids are found. The two latter substances also exist, together with small quantities of tannic acid, in *Galium aparine*.

Pectic acid has only been found in the roots of two plants, the *Cephaëlis ipecacuanha* and *Rubia tinctorum*; it cannot therefore be considered as a characteristic constituent of the plants belonging to the family *Rubiaceæ*. The same is the case with coumarine, which could only be discovered in the herb of *Asperula odorata*.

The same must be said of the organic bases. Bases are contained in four plants,—in *Cephaëlis ipecacuanha* (root), *Chiococca racemosa* (root), *Coffea arabica* (seed) and *Cinchona scrobiculata* (bark). In the other plants no organic bases could be detected. All the plants of this family which were examined contained an acid, the aqueous solution of which,—

a, is coloured dark green by perchloride of iron;

b, becomes brown on the addition of potash, by absorbing oxygen from the air.

c. The acid contains 14 equivs. of carbon and 8 equivs. of hydrogen, with a quantity of oxygen varying from 6 to 10 equivs.

d. All these acids, as far as they have been examined with this view, are decomposed by the action of acids, alkalies and oxygen, or heat, and furnish, with the loss of 2 equivs. of carbon and 2 equivs. of hydrogen, a product of decomposition containing 6 equivs. of hydrogen to 12 of carbon. The oxygen in these products amounts to 5 or 6 equivs.

These acids form a continuous series; they are here placed one below the other, proceeding from the poorest to the richest in oxygen. Some of them possess different properties with the same composition :—

Ipecacuanhic acid $=C^{14}H^{8}O^{6}$, in the root of *Cephaëlis ipecacuanha*.

Caffeotannic acid $=C^{14}H^{8}O^{7}$, in the berries of *Coffea arabica* and the root of *Chiococca racemosa*.

Chinovatannic acid $=C^{14}H^{8}O^{7}$, in the bark of *Portlandia grandiflora*.

Aspertannic acid $=C^{14}H^{8}O^{8}$, in the herb of *Asperula odorata*.

Rubitannic acid $=C^{14}H^{8}O^{9}$, in the herb of *Rubia tinctorum*.

Cinchonatannic acid $=C^{14}H^{8}O^{9}$, in the bark of *Cinchona scrobiculata*.

Galitannic acid $=C^{14}H^{8}O^{10}(?)$, in the herb of *Galium verum*.

The caffeotannic acid is resolved, at an elevated temperature, into pyrocatechine, $C^{12}H^{6}O^{4}$, carbon and water. By the action of the oxygen of the air in the presence of potash, $C^{12}H^{6}O^{5}$ is formed.

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The chinovatannic acid is decomposed by the action of acids into sugar and chinova-red $= C^{12} H^6 O^5$.

The aspertannic acid, by treatment with acids, gives a body of the composition $C^{12} H^6 O^6$.

The cinchonatannic acid, by decomposition in the air, produces cinchona-red, $C^{12} H^7 O^7 = C^{12} H^6 O^6 + HO$.

The tannic acids of the *Galium verum* and *aparine* and of the leaves of *Rubia tinctorum* are contained in these plants in such small quantities, that it was impossible, even by operating upon large quantities of them, to procure sufficient material for the examination of the products of their decomposition. The ipecacuanhic acid also has not yet been examined in this respect.

From what has been here stated, it follows that all the plants of the family *Rubiaceæ* that have been investigated contain a tannic acid of the general formula $C^{14} H^8 O^n$. Taking into consideration the mode of decomposition of these substances, this formula may be written $\left.\begin{matrix} C^{12} H^6 \\ C^2 \ H^2 \end{matrix}\right\} O^n$.

All the *Rubiaceæ* belonging to the division *Stellatæ*, which were investigated, contained, together with the characteristic tannic acids, in all the parts which were examined, rubichloric and citric acids. Rubichloric acid, according to its composition, is immediately allied to these tannic acids; it contains carbon and hydrogen in the same proportion. Its formula is $C^{14} H^8 O^9$; it is decomposed by the action of acids at a high temperature into formic acid and chlorrubine, so that its formula may be written thus:— $\left.\begin{matrix} C^{12} H^6 \\ C^2 \ H^2 \end{matrix}\right\} O^9$. In its properties however it differs completely from the tannic acids; *it is* not coloured green by perchloride of iron, &c.

Citric acid must be considered as a characteristic constituent of the *Stellatæ*, for the same reason that the rubichloric acid is a characteristic constituent of this group. If the hydrate of citric acid be written $= C^{12} H^6 + O^{12}$, it represents a member of the formula $\left.\begin{matrix} C^{12} H^6 \\ C^2 \ H^2 \end{matrix}\right\} O^n$.

Just as the *Stellatæ*, together with the characteristic tannic acids of the formula $\left.\begin{matrix} C^{12} H^6 \\ C^2 \ H^2 \end{matrix}\right\} O^n$, contain the rubichloric and citric acids, analogous in their composition, but differing in their properties, so in the *Cinchonaceæ* the tannic acids are accompanied by kinic and kinovic acids. The kinic acid, $C^{14} H^8 O^8$, like the rubichloric acid, is nearly allied in its composition to the tannic acids of all *Rubiaceæ*, of the formula $C^{14} H^8 O^n$, but like it also differs from them in all its reactions. The place of the citric acid of the *Stellatæ* is occupied in this group by an acid, which, like citric acid, contains 12 atoms of carbon; its formula is $C^{12} H^9 O^3$.

In the true *Coffeaceæ*, *Cephaëlis ipecacuanha*, *Coffea arabica* and *Chiococca racemosa*, no common characteristic substance accompanies the tannic acids. In the seeds of *Coffea arabica*, the citric acid of the *Stellatæ* is present, although in inconsiderable quantity; the

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kinovic acid of the *Cinchonaceæ*, combined with hydrate of carbon, is contained in the root of *Chiococca racemosa* in the form of *caincic acid*. In the root of *Cephaëlis ipecacuanha* both acids are wanting. The large quantity of starch and gum, which partake of the formula $C^{12}H^{10}O^{10}$, contained in this plant, is perhaps to be regarded as the representative of the citric acid. Citric acid (anhydrous) with 2 additional equivs. of water $=C^{12}H^{7}O^{13}$, is starch or gum in which 3 equivs. of hydrogen are replaced by 3 equivs. of oxygen.

If the plants of these three groups be brought together with their characteristic constituents, the following tabular view is obtained:—

RUBIACEÆ.

I. *Stellatæ.*

I. Characteristic constituent.	II. Characteristic constituent.	III. Characteristic constituent.
Tannic acid of the formula— $\left.\begin{matrix}C^{12}H^{6}\\C^{2}H^{2}\end{matrix}\right\}O^{n}$. n=8, 9 or 10.	Rubichloric acid— $\left.\begin{matrix}C^{12}H^{6}\\C^{2}H^{2}\end{matrix}\right\}O^{9}$.	Citric acid— $C^{12}H^{6}O^{12}$.

II. *Cinchonaceæ.*

I. Characteristic constituent.	II. Characteristic constituent.	III. Characteristic constituent.
Tannic acid of the formula— $\left.\begin{matrix}C^{12}H^{6}\\C^{2}H^{2}\end{matrix}\right\}O^{n}$. n=7 or 9.	Kinic acid— $\left.\begin{matrix}C^{12}H^{6}\\C^{2}H^{2}\end{matrix}\right\}O^{8}$.	Kinovic acid— $C^{12}H^{9}O^{8}$.

III. *Coffeaceæ.*

I. Characteristic constituent.	II. Characteristic constituent.	III. Characteristic constituent.
Tannic acid of the formula— $\left.\begin{matrix}C^{12}H^{6}\\C^{2}H^{2}\end{matrix}\right\}O^{n}$. n=6 or 7.	Wanting.	Citric acid $=C^{12}H^{6}O^{12}$, or Kinovic acid $=C^{12}H^{9}O^{8}$, or Gum and starch $=C^{12}H^{10}O^{10}$.

As regards the quantity of the characteristic tannic acids existing in the different groups, the largest quantity is found in the *Coffeaceæ* and *Cinchonaceæ*, although for the most part already changed by the influences to which the parts of the plants have been exposed before they reach us. In the *Stellatæ* the quantity of these acids is very small, especially in *Galium aparine* and the leaves of *Rubia tinctorum*.

If these tannic acids be considered with regard to their amount of oxygen, it appears that this is greatest in those plants which inhabit the temperate zones, such as the *Stellatæ*, or which grow at greater elevations, like the *Cinchonæ*, which flourish on the Andes at from 4000 to 8000 feet above the level of the sea; whilst it is small in the tannic acids of plants inhabiting hot climates, such as *Cephaëlis ipecacuanha*, *Coffea arabica* and *Chiococca racemosa*. Whilst the tannic acids of the *Stellatæ* contain 8–10 equivs. of oxy-

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gen, those of the true *Coffeaceæ* have only 6–7 equivs.; so that the deoxidation goes further in high temperatures than in colder climates.

With regard to those plants, which, together with a tannic acid, contain also an acid of the formula $C^{14} H^8 O^n$, it appears that they only differ in their composition by 1 equiv. of oxygen, so that by the separation of 1 equiv. of oxygen, the one acid might pass into the other. Their different properties and mode of decomposition sufficiently show that they are not to be considered as different oxides of the same radical. The author here compares together the acids which are contained in the same plant.

The tannic acid in *Portlandia grandiflora*, $C^{14} H^8 O^7$, may be formed from the kinic acid, $C^{14} H^8 O^8$, by the loss of 1 equiv. of oxygen; as may the kinic acid, $C^{14} H^8 O^8$, of the *Cinchona scrobiculata* from its cinchonatannic acid, $C^{14} H^8 O^9$; the aspertannic acid, $C^{14} H^8 O^8$, of the *Asperula odorata* from its rubichloric acid, $C^{14} H^8 O^9$; and the rubichloric acid, $C^{14} H^8 O^9$, of the *Galium verum* from its galitannic acid, $C^{14} H^8 O^{10}$.

The rubitannic acid of the *Rubia tinctorum* may pass directly into the isomeric rubichloric acid. The occurrence of acids with 12 equivs. of carbon, such as citric and kinovic acids, together with acids of the formula $C^{14} H^8 O^n$, as well as, on the other hand, the readiness with which the acids containing 14 equivs. of carbon pass into substances with 12 equivs. of carbon, appears to render it probable that these acids with 12 equivs. of carbon are the materials from which the acids with 14 equivs. are formed, although hitherto no one has succeeded in forming a tannic acid from citric or kinovic acid.

If the hydrate of citric acid, $C^{12} H^6 O^{12}$, were to assimilate 1 equiv. of formic acid and give off oxygen, the formation of the tannic acids of the *Rubiaceæ* might be effected,—Citric acid $= C^{12} H^6 O^{12} + C^2 H^2 O^4$, formic acid $= C^{14} H^8 O^{16}$.

$C^{14} H^8 O^{16} - O^6 = C^{14} H^8 O^{10}$, the tannic acid of *Galium verum*.

$C^{14} H^8 O^{16} - O^7 = C^{14} H^8 O^9$, the rubichloric acid of the *Stellatæ*, or the tannic acids of the cinchona bark and of *Rubia tinctorum*.

$C^{14} H^8 O^{16} - O^8 = C^{14} H^8 O^8$, the kinic acid of the *Cinchonaceæ*, or the tannic acid of *Asperula*.

$C^{14} H^8 O^{16} - O^9 = C^{14} H^8 O^7$, caffeotannic acid, or the tannic acid of the *Cinchona nova* bark.

$C^{14} H^8 O^{16} - O^{10} = C^{14} H^8 O^6$, the tannic acid of the *Ipecacuanha* root.

In this manner the kinovic acid, $C^{12} H^9 O^5$, might be transformed into these acids by the assimilation of oxalic acid and oxygen, $C^{12} H^9 O^5 + C^2 O^3 = C^{14} H^9 O^6$. If 1 equiv. of water be separated, there remains $C^{14} H^8 O^5$, which united with 1 equiv. oxygen might form ipecacuanhic acid, with 2 equivs. the caffeotannic acid, and so on.

That kinovic acid is capable of assimilating other compounds is shown by the investigation of caincic acid, which consists of kinovic acid united with a hydrate of carbon, which has the constitution of acetic acid.

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$C^{16} H^{13} O^7$, caincic acid $= C^{13} H^9 O^3$, kinovic acid $+ C^4 H^4 O^4$.

Rubichloric acid, and its separation into chlorrubine and formic acid, is a proof that a process like that above mentioned really takes place in the plants. Citric acid $= C^{12} H^6 O^{12}$, loses 7 equivs. of oxygen and passes into $C^{12} H^6 O^5$, which, united with the elements of formic acid, produces rubichloric acid.

$C^{14} H^8 O^9$, rubichloric acid $= C^{12} H^6 O^{12}$, citric acid $- O^7 + C^2 H^2 O^4$, formic acid.

At a low temperature the deoxidation of the citric acid appears to take place very imperfectly. The herb of *Richardsonia scabra*, which was cultivated last summer by Prof. Kosteletzky in the Botanic Garden of Vienna, contained inconsiderable quantities of tannic acid, whilst not a trace appeared in the roots; both herb and root, on the other hand, were rich in citric acid salts. In its native country, the root of the *Richardsonia scabra* contains tannic acid.

The author here adds some considerations on the origin of the hydrates of carbon, and particularly on the question from what substances they are produced. The fact that plants possess the faculty of separating oxygen by the agency of the sunlight, after they have absorbed carbonic acid and water, induced Liebig to suppose that the hydrates of carbon were formed from acids. The absorption of carbonic acid and water and the elimination of oxygen take place by degrees, and thus from compounds rich in oxygen, but poor in carbon and hydrogen, constituents are gradually formed, always richer in carbon and poorer in oxygen.

The author considers the results of his investigation to support Liebig's view, for it proves that the external resemblance in the form of the plant corresponds also constantly with the acids combined with various bases in its interior. It is also in favour of this supposition that the hydrates of carbon are really formed by the process of deoxidation in the plants, that acids occur in the same plant, which with the same amount of carbon and hydrogen are distinguished from one another by containing a larger or smaller quantity of oxygen. Although these acids cannot be regarded as different oxides of one radical, it appears to the author to be extremely probable that they may arise from the deoxidation of one another.—*Bericht der Akad. der Wissensch. zu Wien Math. Phys. Cl.*, Jan. 1852.

On the Production of Photographs on Glass. By J. Pucher.

According to this process, a thin film of iodide of sulphur is formed upon plate glass, by covering the glass, which must be perfectly clean, with a very thin coating of sulphur, and then impregnating this for a few seconds with the vapour of iodine. The glass plate is then placed in the camera, where at the same time the vapour of some quicksilver in an iron cup in the bottom of the camera acts upon the iodide of sulphur with which it is coated, and it receives the photographic image within a minute. The glass plate, when

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taken out of the camera, only exhibits a trace of the picture, but this immediately comes out on exposure to the action of the vapour of bromine. If the picture be now held over alcohol, and some of the same liquid be poured upon it, it will be fixed. Not more than from five to eight minutes are required for the whole operation.

The glass plates must be breathed upon and well rubbed with soft linen rag several times before use. They are coated with sulphur by burning sulphur sticks, made on purpose, in a proper tube, and holding the plates over it at a distance of about 3 inches. These sulphur sticks are prepared by dipping pieces of rush-pith into a melted mixture of sulphur and mastic, with which they become incrusted. For use, these sulphur sticks, which are about the size of a lucifer match, are stuck on a brass needle, introduced into the middle of a glass tube and kindled, so that the vapour of the sulphur may come in contact with the glass plate held over it.

These glass plates are so sensitive, that the coating of iodide of sulphur becomes instantly changed on exposure to direct sunlight, and give a Moser's image within five minutes when laid in a book. The figures thus obtained are most easily read by candlelight. In daylight, the blue letters can be recognised on the yellow ground only by looking through the plate towards the middle of the window, or towards a sheet of paper fastened in that place, the sulphur not having been removed either by vapour of bromine or by alcohol.

If a glass plate, covered with a solution of gum and exposed to the vapour of iodized sulphur, be placed in the camera, a positive picture, with all its details, is obtained, the outlines of which can be laid bare by an etching-point capable of scratching the glass. If a glass plate, so marked, be rubbed in with printing ink, the outlines will be filled, and the ink will remain in them when the glass is freed from the coating of gum by means of water. The picture is then easily transferred to paper, which is to be laid on the plate and rubbed over with a paper-knife.—*Archiv der Pharm.*, lxix. p. 301.

On Cystic Oxide Calculi. By J. Müller.

Two cystic oxide calculi have occurred to the author within a short time. One of these stones weighed 280·90 grs. It was of the size of a green walnut, hollow within, and contained enclosed in a wide space a free kernel of the size of a broad bean, weighing 39 grs. and consisting of pure cystine. In the shell, which was of unequal thickness, being on one side only 2–3 lines, on the other ½ an inch thick, four different layers could be observed,—1st, an inner reticulated layer of a yellowish-white compact substance; 2nd, a layer of very white cystine; 3rd, a very remarkable thin layer of a black colour, enclosing the entire stone; and 4th, beautifully crystallised white cystine. The black layer evolved sulphureted hydrogen when treated with muriatic acid. The stone was obtained by operation from a man of seventy-three years old.

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Another stone, taken from the bladder of a boy six years and a half old, weighed 268 grs., and had a specific gravity of 1·58. Its form was oval, somewhat depressed; its colour yellowish-white. Its longitudinal section showed a confused crystalline texture, with a white layer on the periphery.

The inner part of a fragment of the concretion was subjected to a quantitative analysis. This gave—

Urate of ammonia	26·25
Uric acid	2·50
Cystine	55·55
Phosphate of ammonia and magnesia, with traces of phosphate of lime	7·50
Water	7·50

By means of the microscope the author detected the continuance of the formation of cystine in the urine, eight weeks after operation.—*Archiv der Pharm.*, lxix. 297 and 328.

On the Behaviour of the Nitrogenous Compounds of Sugar with Reducing Agents. By Ad. *and* W. Knop.

We have for some time past been engaged in endeavouring to effect the decomposition or metamorphosis of nitroglucose and nitromannite by reducing agents. The sulphite of ammonia and protochloride of copper appeared, from several preliminary experiments, to be well adapted for the purpose. We have already published a short notice upon this subject; the complete results obtained are as follows:—

1. *Nitroglucose.*—It is prepared according to the known process. If it be allowed to lie under water in the summer, it becomes soft, and capable of being kneaded, clings to the fingers, and when laid upon a glass plate in the air and pressed with another glass plate, it gives off uninterruptedly a fluid, which is rendered strongly acid by the presence of nitric acid. At the same time it evolves no nitrous fumes. If it be put into a mixture of alcohol and æther, it is dissolved, but it is only with a certain proportion of the two fluids that a homogeneous solution is obtained; with other proportions a solution is produced which separates into two colourless strata. If the fluid produced in either case be boiled several hours with sulphite of ammonia, the saccharine compound will be tolerably completely decomposed; the period when this takes place may be known by the solution, when poured into water, no longer producing any turbidity or any film of nitroglucose.

The complete decomposition of the nitroglucose is however not so easily attained in this way. The gas which is evolved in this experiment was collected and examined. It consisted of sulphite of ammonia, æther and vapour of alcohol, nitrite of oxide of æthyle, carbonate of ammonia, and principally of nitrogen gas, which, according to the duration of the boiling, was always mixed with more or less nitric oxide. The fluid, if a perfectly saturated sulphite of ammonia be employed, remains completely colourless.

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In the other process, the nitroglucose is to be dissolved in a mixture of alcohol and æther, and an ammoniacal solution of a quantity of chloride of copper, more than sufficient for its decomposition, added to it; the flask in which the experiment is performed is to be filled nearly to the stopper, which is to be provided with a gas-tube, the other end of which dips into water; the whole apparatus is now to be placed in the sun, when at the same time that the æther boils a proportionably small quantity of gas will escape. When the solution has been allowed to stand two days in the sun, it is heated in the water-bath until the complete decomposition of the saccharine compound, which proceeds in this case much more rapidly than in the experiment with sulphite of ammonia, and is completed after a short boiling. The whole of the gas evolved during the decomposition of 5 grms. of nitroglucose amounted to about 4 or 5 cubic inches, and contained therefore no constituent portion of the products of the decomposition of the sugar, in a proportion corresponding with the quantity of sugar employed.

The gas contained æther and vapour of alcohol, with a small quantity of carbonate of ammonia. After long-continued washing with water and mixing with its own volume of water, it could not be ignited in the eudiometer by the spark. This gas was principally nitrogen; the vapour of æther, which goes over with it at first, is always mixed with a small quantity of nitrous æther.

When the nitroglucose has been treated with sulphite of ammonia, the resulting fluid contains sulphate, nitrate, nitrite and carbonate of ammonia. When it is treated with protochloride of copper, the oxidizing action of the nitroglucose is immediately perceptible in the increasing depth of colour of the ammoniacal solution, which is at first pale, but becomes rapidly deep blue. After the reaction, we find with the excess of protochloride of copper, ammoniochloride of copper, carbonate of ammonia and a large quantity of nitrite of ammonia. If the fluid, therefore, whether the operation has been performed with sulphite of ammonia or with ammoniacal solution of protochloride of copper, be allowed to boil for a long time after the complete decomposition of the sugar, nitrogen gas will be continually evolved in consequence of the decomposition of the nitrite of ammonia.

The alcoholic solution was now distilled, but no new substance, or substance formed by the decomposition of the sugar, except a small quantity of nitric æther, was found. In the residue, and also in that which remained after spontaneous evaporation, we determined the acids and the bases.

The fluid procured by treating with protochloride of copper was freed from copper by sulphuret of ammonium; the only salt which crystallized from it was muriate of ammonia; nitrite of ammonia was recognised by the evolution of gas on the water-bath. If the fluid was then evaporated to dryness with chalk, quick-lime or carbonate of lead, and the mass extracted with water, nitric and nitrous acid salts were procured, but no salt of any organic acid; and even the fluid, after neutralization with an acid and expelling the carbonic

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acid, gave no precipitate with neutral salts of the same bases, so that no organic acids are formed.

We supposed, therefore, that in the decomposition of this nitro-compound, the carbonic acid transferred itself to the ammonia. In order to ascertain what became of the carbon of the sugar, we dissolved 5 grms. of nitroglucose in a mixture of æther and alcohol, added to it a filtered solution of chloride of calcium in ammonia, then the perfectly clear solution of protochloride of copper in ammonia, and effected the decomposition by boiling in the water-bath. With the commencement of the decomposition, carbonate of lime was thrown down together with protochloride of copper; this was filtered off, and half the solution allowed to evaporate spontaneously. To the concentrated residue oxalic acid was added, which immediately evolved a quantity of brown nitrous fumes, and precipitated all the lime and all but a trace of the copper. It was now allowed to evaporate further spontaneously, and the residue dried; it was found to consist of oxalate of ammonia, with a slight admixture of chloride of ammonium.

The other half of the solution was supersaturated with nitric acid, and allowed to stand a long time in the air to free it from nitrous acid; it was then distilled with an excess of quick-lime, and the result of the distillation received in muriatic acid. This solution was evaporated to dryness, and precipitated in four fractions with chloride of platinum, in order to determine the presence of volatile bases. All four precipitates however contained between 43·4–44·4 per cent. of platinum; no volatile base, therefore, was present with the ammonia.

Nitromannite.—If concentrated sulphuric acid, diluted with from 2–4 per cent. of water, be poured, after the mixture has cooled in a flat dish, over some nitromannite in a large beaker, and this covered with a glass plate, the interior of the glass is filled with strongly acid, colourless fumes of nitric acid.

Nitromannite is only decomposed by sulphite of ammonia after six to eight hours' boiling for 5 grms.; there was always, however, some undecomposed nitromannite in the residue. The liquid contained a large quantity of sulphate of ammonia; in other respects the phænomena were the same as in the case of nitroglucose. If a mixture of sulphite of ammonia and ammoniacal solution of protochloride of copper be employed, the oxidizing property of the nitromannite is distinctly observable in the change of the red sulphite of the protoperoxide of copper first formed, into blue ammonio-perchloride of copper. All the results were the same as in the preceding, only differing in the fact, that in this case unmistakeable mannite was reduced from nitromannite perfectly free from mannite; according to this, the fact formerly published by us, that solutions of nitromannite, rendered acid by muriatic acid, furnish reduced mannite on being treated with metals, is confirmed, as well as the later statement of Dessaignes, that sulphuret of ammonium reduces nitromannite. That we did not succeed formerly in reducing nitromannite in the latter manner may perhaps have arisen from our not having

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employed ammonia completely saturated with sulphureted hydrogen, and having consequently obtained brown products of decomposition. Coloured solutions are also produced with sulphite of ammonia if the ammonia be not perfectly saturated with sulphurous acid.

Taking all the products of the decomposition into calculation, it results that in the reduction of nitroglucose, only carbonic acid and water, and apparently ammonia, are formed. In a fluid to which chloride of calcium was previously added, the quantity of carbonate of lime precipitated amounted indeed to much less than was required to correspond with the quantity of carbon contained in 5 grms. of sugar; but carbonate of ammonia was always evolved during the decomposition in company with the nitrogen gas, and we therefore concluded that the large quantity of chloride of ammonium and nitrate of ammonia, which, as is well known, on being boiled with freshly-formed carbonate of lime, expels the carbonic acid, was the cause of our obtaining much too little carbonate of lime. An explanation of this decomposition is very possible. If nitromannite consists of $C^{12} H^8 O^6 + 6NO^5$, we have—

$$C^{12} H^8 O^6 + 6NO^5 = C^{12} H^8 N^6 O^{36}$$

$$C^{12} H^8 N^6 O^{36} + 4HO = 12CO^2 + 3NH^3 + 3N + 3HO + O^{15}$$
$$= 12CO^2 + 2(NH^4 O, NO^5) + NH^4 O, NO^5.$$

Nitrite of ammonia furnishes nitrogen on its decomposition by heat; the nitrate of ammonia may be further reduced by sulphurous acid, and also by protochloride of copper. The decomposition of the nitroglucose may be regarded as precisely similar.—*Pharm. Cent. Blatt.*, xxiii. p. 423.

On the Presence of Trimethylamine in the Extracted Juice of Salt Herrings. By M. Hofmann.

In a former paper I expressed the opinion, that the base described by M. Wertheim by the name *œnylamine* or *propylamine* might possibly be identical with *trimethylamine*:—

$$\left.\begin{matrix} H \\ H \\ C^6 H^7 \end{matrix}\right\} N = \left.\begin{matrix} C^2 H^3 \\ C^2 H^3 \\ C^2 H^3 \end{matrix}\right\} N = C^6 H^9 N.$$

The interesting observation, likewise due to M. Wertheim, that this substance is also met with in pretty considerable quantity in the liquid which gradually separates from salted herrings, has formed the starting-point for some experiments which have lately been made to solve this question. According to the experiments of H. Winkles, the predominating substance in the mixture of several bases furnished by the extracted juice of salt herrings is *trimethylamine*. The identity of this substance with trimethylamine prepared synthetically was proved, not merely by the direct comparison of the two substances, but also by the characteristic reaction of the iodide of methyle. With the latter the base in question immediately furnished a paste of crystals of iodide of tetramethylammonium.

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It appears therefore exceedingly doubtful whether the true propylamine has yet been obtained. It also shows the necessity of demonstrating by experiment how far we are authorized in giving to petinine the name of butylamine, which has been assigned to it of late by several chemists. The behaviour of this substance with iodide of methyle or æthyle would easily furnish a solution of this question.—*Comptes Rendus*, July 12, 1852.

On Gallic Acid Fermentation. By M. Robiquet.

Gall-nuts contain, besides tannin and the several principles which have already been pointed out by chemists, pectose and pectase. The latter ferment, which exists both in the soluble and in the insoluble state, acts at the same time upon the pectose and upon the tannin, converting the first into pectine and the second into gallic acid. The presence of water and a temperature of 77° to 86° F. are requisite for this reaction, which resembles in every respect the ordinary phænomena of fermentation.

The ordinary tannin, which has been prepared with æther, contains sufficient pectase to pass spontaneously in the presence of water into gallic acid; but if care has been taken to purify it, or if its solution has been simply boiled for a few minutes, the change no longer takes place.

Synaptase, yeast, vegetable and animal albumen, and legumine have a very doubtful action upon tannin, and retard rather than accelerate its conversion into gallic acid.

It is quite as easy to convert the pectine of fruits into pectic acid by means of the pectase obtained from gall-nuts, as to convert tannin into gallic acid with pectase separated from the juice of fresh roots, and especially from turnips.—*Comptes Rendus*, July 5, 1852.

ANALYTICAL CHEMISTRY.

On the Action of Baryta and Strontia on Compounds of Titanium before the Blowpipe. By E. J. Chapman, *Professor of Mineralogy in University College, London*.*

All chemists are familiar with the fact, that compounds of titanium fused with borax before the blowpipe impart to the glass in a reducing-flame a dark amethyst colour; and that the bead becomes opake, and of a light blue tint, when subsequently exposed for an instant to the point of an oxidating flame, owing to the production and precipitation of a portion of titanic acid.

This reaction however does not take place in the presence of baryta. If a sufficient amount of titanic acid, for instance, be fused with borax, so as to produce with a reducing-flame a glass which

* Communicated by the Author.

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on cooling appears almost black from the intensity of its colour, and to this a portion of baryta be added, the colour of the bead will not be affected by the addition; but it will be found that the glass cannot afterwards be rendered light blue and opake by the action of an oxidating or intermittent flame. The colour may be gradually driven off, but no precipitation of titanic acid, and consequently no opacity will occur. A comparatively small amount of baryta is sufficient to affect the reaction in a very evident degree; and with a larger quantity, the reaction is destroyed, and the formation of a milky or blue enamel entirely prevented. Care must, of course, be taken, in verifying this assertion, that the borax-glass be not oversaturated, as baryta in great excess would necessarily of itself render the bead opake.

I have tried if a similar result can be produced by the employment of other substances, as potash, lithia, strontia, lime, magnesia, oxide of zinc, alumina, silica, &c.; but, except in the case of strontia, I cannot find that any change ensues from the presence of these bodies. The effect, moreover, produced by strontia is by no means so characteristic as that obtained by baryta. A much larger quantity of the reagent is required, for instance, to produce the same result.

The cause of this peculiarity is not very easily explained; for the glass may be rendered equally clear and colourless (or bright yellow if the TiO^2 be present in considerable quantity) after, as before the addition of the modifying substance, although it cannot be made opake or be transformed into an enamel after such addition. May not, however, the phænomenon be accounted for on the following supposition, namely, that titanate of soda exacts a higher or more continued temperature for its production before the blowpipe than is required for the formation of titanate of baryta, so that, in the pure borax glass, the portion of titanic acid which is separated from the oxide or sesquioxide of titanium by the brief action of the oxidating flame, is rendered visible; whereas, in the baryta-glass, this portion, in separating, combines immediately with the baryta, or with a portion of it, and the resulting salt is at once dissolved?

The above results are rendered far more striking if pure borate of baryta be employed for the experiment in place of the mixed borates.

On the Testing of the Metallic Spots deposited by burning Hydrogen on Porcelain. By H. Wackenroder.

A new method of distinguishing arsenical and antimonial spots was some time since proposed by Slater*. Wackenroder has tried this method, and published the following observations on the mode of determining arsenic by separation from arseniureted hydrogen.

If the hydrogen gas produced by the action of diluted pure or ordinary purified sulphuric acid upon common zinc be kindled, and the strong current of gas directed against white earthenware, a black

* Chem. Gaz., vol. ix. p. 57.

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spot of lead will be produced by the reduction of the lead-glazing of the earthenware.

If a very strong current of hydrogen gas be developed, and no deposit of metal takes place from its flame upon porcelain, we may feel perfectly sure of the purity of the gas.

But if muriatic acid be employed instead of sulphuric acid for the production, or if any chloride exists in the fluid used, metallic spots may be formed during the rapid evolution of the gas, which however are only spots of zinc. They are distinguished in this manner, that on pouring over them diluted muriatic acid, they rapidly disappear, and that they are also readily removed by means of hypochlorite of soda.

To avoid error, it is also necessary that no nitric acid or sulphuret be present in the apparatus used in the development of the gas, which may be best formed of a two-necked bottle with a funnel-tube and a tube bent at right angles and drawn to a point, for the passage of the gas. The nitrous acid formed in the one case readily decomposes antimoniureted and arseniureted hydrogen gas, whilst a sulphuret readily causes the formation of some sulphuretted hydrogen gas, by which the spots of arsenic and antimony receive more or less of a reddish or yellowish colour.

Granulated zinc with dilute sulphuric acid evolves hydrogen gas better than pieces of crystalline zinc. The evolution of gas, however, easily becomes so violent that it must be moderated by the addition of water. When it has gradually become weak, it may be remarkably enlivened, frequently even to a most violent degree, by the addition of a small quantity of a solution of arsenious or arsenic acid. This circumstance must therefore not be neglected in the employment of Marsh's apparatus in judicial investigations.

1. *Arsenical Spots.*—When sufficient hydrogen gas has been generated to expel the atmospheric air from the bottle, the fluid or substance (such, for instance, as a piece of green paper) which is to be examined for arsenic is introduced into it. If there be a funnel-tube to the flask, the addition of small quantities of the liquid to be examined to the sulphuric acid employed to generate the gas is readily effected by stopping the gas-tube with the finger, so that as much acid rises into the funnel as it can hold. The arsenical spots produced on the porcelain are rapidly dissolved by pouring over them hypochlorite of soda, and the porcelain becomes perfectly clean; on the other hand, the spots do not disappear on being poured over with dilute muriatic acid. If the spots of arsenic be shining, and consequently proportionately thick, the hypochlorite of soda is somewhat longer in effecting their solution, which however it always does in a period of not more than a few seconds.

2. *Antimonial Spots.*—If a little tartar-emetic (or any other compound of antimony) be added to the mixture of zinc and sulphuric acid in the flask, antimoniureted hydrogen is immediately given off with the hydrogen. Whilst the spots on the porcelain are still faint and of a dull appearance, they are acted upon, after some time, by hypochlorite of soda, in such a manner that they become gradually

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indistinct, rather by being washed off by the alkaline fluid, than in consequence of becoming dissolved in it. But if the antimonial spots be black and shining, and consequently more firmly fixed on the porcelain, they completely withstand the action of both hypochlorite of soda and diluted muriatic acid, but are quickly dissolved by a mixture of the two liquids.

3. *Arsenical Spots containing Antimony, and Antimonial Spots containing Arsenic.*—If an arsenical fluid containing antimony be introduced into the gas apparatus, the spots on the porcelain at first contain principally only arsenic, apparently in consequence of the antimony being less volatile; but if shining spots be produced on the porcelain, which contain more antimony, these resist the action of hypochlorite of soda in a greater or less degree, and are often only eaten away round the edges.

Small quantities of antimony in the arsenical spots render these strong and more shining, but do not prevent their solution in hypochlorite of soda. The hypochlorite of soda may therefore be used with the greatest certainty in distinguishing purely arsenical from purely antimonial spots, which indeed is the principal point in judicial investigations, but not in detecting a trace of antimony in arsenical spots; it also serves in some measure to detect traces of arsenic in antimonial spots. It might be possible, but probably useless in practice, to ascertain by comparative investigations the quantitative proportions of arsenic and antimony at which distinct differences occur in the behaviour of mixed metallic spots with hypochlorite of soda.—*Archiv der Pharm.*, lxx. p. 14.

On the Determination of Nitrogen. *By* M. Ullgren.

The author's method consists in converting the nitrogen into ammonia by the combustion of the substance under examination with soda-lime, and ascertaining the quantity of ammonia by directly weighing the apparatus. The apparatus consists of two U-tubes. The first contains a layer of asbestos in the arm which is turned towards the combustion-tube; this is placed at the top, at the point where the products of the combustion enter; and at the bottom, nearly in the other arm, several pieces of caustic alkali of the size of peppercorns; this other arm is then completely filled with small fragments of india rubber, for the purpose of absorbing carbureted hydrogen. This U-tube is entirely immersed in water, which is kept at a temperature of 140°–158°, so that the ammonia may not be retained in the tube. This U-tube is followed by that in which the ammonia is to be fixed. The means of absorption consist of pieces of anhydrous sulphate of zinc, with which the tube is to be filled. It is to be weighed before and after the operation; the difference is exactly the quantity of ammonia produced, from which the nitrogen is calculated. At the conclusion of the combustion, the produced hinder part of the combustion-tube is to be broken off, and about 50 cubic inches of air drawn through the apparatus by means of an aspirator.—*Journ. für Prakt. Chem.*, lv. 21.

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THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Meconic Acid, and some of its Derivatives.

By Mr. HENRY HOW, *Assistant to* Dr. Anderson*.

IN a paper on comenic acid†, I mentioned my being engaged in an investigation on meconic acid; the details of the experiments referred to form the matter of the present communication.

My object in undertaking this subject was to ascertain if products corresponding to those described as derived from comenic acid were formed under similar circumstances in the case of meconic acid. I also thought it probable, that as the former is itself a derivative of the latter, the changes undergone by meconic acid in some reactions would be found to result in substances apparently the immediate derivatives of comenic acid. This remark refers to the action of heat on meconate of ammonia, and it will be seen that the expectation was realized. A similar result was found in other instances, where it had not been anticipated.

The experiments I am about to detail were performed in the laboratory of Dr. T. Anderson.

The process employed for the purification of meconic acid was that given by Gregory in his 'Outlines,' excepting that ammonia was substituted for potash as the solvent of the crude acid. As in the case of comenic acid, the volatile alkali was preferred, because, although in both cases a great deal of acid remains in the highly-coloured mother-liquors, from which it can only be recovered in a pure state at the expense of much time and labour, it was found that if ammonia was used, the whole of the mother-liquors could be employed under circumstances where their impure state did not affect the results of the experiment. A considerable saving was thus effected. This point is of some importance, because the numerous solutions requisite for the purification of meconic acid occasion so much loss, that seldom much more than a fourth part of the weight of the crude acid started from is obtained as the result of a careful preparation.

The process consists in dissolving crude meconic acid in hot water by aid of caustic ammonia. The crude acid is obtained from me-

* From the Transactions of the Royal Society of Edinburgh, vol. xx. part 3.

† Transactions of the Royal Society of Edinburgh, vol. xx. part 2; and Chem. Gaz., vol. ix. p. 328.

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conate of lime by treating it three successive times with 20 parts boiling water and 3 parts strong muriatic acid. The mixture of the acid so obtained, and about twice its weight of water, is kept hot in a water-bath and constantly agitated, till, by the addition of caustic ammonia, solution is complete; the salt formed is extremely soluble in hot water, and the fluid cools to a solid mass. The black mother-liquor is squeezed out by strong pressure, and the cake of salt redissolved twice or thrice in as small a quantity of boiling water as is found sufficient, the mother-liquors being always pressed from the crystallized salt. By proceeding in this manner, a perfectly white salt is obtained, from whose solution in hot water an excess of strong hydrochloric acid throws down the meconic acid in colourless brilliant scales; these require but a little washing with cold water, and one resolution in the smallest possible quantity of hot water, to be obtained on cooling of the fluid absolutely pure. This is another advantage in the use of ammonia, for the potash salt requires, at the least, three treatments with acid to abstract the alkaline base entirely.

Bibasic Meconate of Ammonia.—The ammonia salt obtained in the above-given process crystallizes from tolerably dilute fluids left at rest in groups of radiated fine silky needles; they have an acid reaction. In the following analysis the nitrogen was determined by adding hydrochloric acid to a solution of the salt, evaporating the filtrate with some bichloride of platinum, collecting the residue on a filter, and washing with alcohol and æther; the per-centage of nitrogen was calculated from the platinum remaining on ignition of the undissolved ammonia salt. This method was preferred in one or two other cases of ammonia salts, as more convenient than a combustion with soda-lime, and less liable to loss; for it is not easy always to mix these salts with soda-lime so quickly as to avoid the escape of ammonia:—

Carbon	35·51	14 =	84	35·89
Hydrogen	4·73	10	10	4·27
Oxygen	..	14	112	47·88
Nitrogen.....	12·09	2	28	11·96

The hydrogen is rather above the calculated result; but the substance, when dried at 212°, is extremely hygroscopic. The numbers lead to the formula $HO, 2NH^4O, C^{14}HO^{11}$, as representing the constitution of bimeconate of ammonia in the dry state. The crystals appear to contain varying amounts of water of crystallization, as numbers were obtained in drying different specimens indicating a loss of between 6 and 16 per cent. of water. An aqueous solution of this salt may be boiled without any change; but when kept for a considerable time boiling with an excess of ammonia, it becomes altered.

Action of Heat on Meconate of Ammonia.

Comenamic Acid.—Some of the highly-coloured mother-liquors of the purifying process were retained at or near the boiling temperature for some hours, ammonia being kept present in excess. The addition of hydrochloric acid to the cooled fluid caused copious evo-

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lution of carbonic acid, and when added in proper quantity, a considerable precipitate. By repeated crystallizations from boiling water, and the use of pure animal charcoal, the precipitated substance was obtained in colourless shining scales. The following is its analysis before being rendered absolutely pure:—

Carbon	45·84	12 =	72	46·45
Hydrogen	3·51	5	5	3·22
Oxygen	..	8	64	41·30
Nitrogen.....	8·67	1	14	9·03

The results of which are sufficient to show this body to have the composition of comenamic acid; the characters and reactions of the acid left me no doubt as to its identity with that derived from comenate of ammonia under similar circumstances. It may be considered as formed from the bibasic meconate of ammonia, in the presence of an excess of ammonia, by the elimination of 2 equivs. carbonic acid, 2 of water and 1 of ammonia, as in the equation—

$$HO, 2NH^4O, C^{14}HO^{11} = C^{12}H^5NO^8 + NH^3 + 2HO + 2CO^2.$$

This offers a convenient source of comenamic acid, as very impure meconic acid may be employed.

Action of Chlorine on Bibasic Meconate of Ammonia.

A current of chlorine gas passed through some of the coloured mother-liquor of the above salt, deprived it of colour considerably, and caused a speedy deposit of hard granular crystals adhering to the sides of the vessel. This was collected, and recrystallized from boiling water; it was found to be not very soluble, and the fluid on cooling deposited the substance in hard crystals, which on being magnified were seen to consist of thick needles radiating from a centre. It contained no chlorine, and proved to be an ammonia salt of meconic acid containing 1 equiv. of alkaline base. I am not aware that this salt has been obtained before; I therefore subjoin an analysis of it:—

Carbon	38·57	14 =	84	38·70
Hydrogen	3·55	7	7	3·22
Oxygen	..	14	112	51·63
Nitrogen.....	6·21	1	14	6·45

which gives as the formula of the monobasic meconate of ammonia, as dried at 212°, $2HO, NH^4O, C^{14}HO^{11}$. The crystallized salt contains 7·70 per cent. of water, which is equal to 2 equivs.; 7·65 is the number corresponding to the formula $2HO, NH^4O, C^{14}HO^{11} + 2Aq$.

The original mother-liquor of this salt deposited a further quantity of the same on being concentrated, and by continued evaporation a few crystals of a different appearance were obtained; when these were separated, and recrystallized from boiling water, they presented themselves in the form of long square prismatic needles. In their appearance, and a few reactions, they showed the characters of chlorocomenic acid. A determination of the chlorine is, I think, sufficient to prove that the crystals really consist of this

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acid:—3·315 grs., dried at 212°, gave, after burning with lime, 2·505 grs. chloride of silver. The per-centage of chlorine, calculated from this experiment, is 18·69, which agrees very closely with 18·63, the number corresponding to the formula of chlorocomenic acid in the dry state:—$2HO, C^{12} \left\{ \begin{matrix} H \\ Cl \end{matrix} \right\} O^8$.

Oxalic acid is found in the last mother-liquors of this process.

Action of Bromine on Meconic Acid.

Bromocomenic Acid; Carbonic Acid.—I had no doubt of finding the action of bromine closely similar to that of chlorine on meconate of ammonia; but it occurred to me it would be more readily learned from employing the acid itself, whether it gave a substitution product, or whether its molecule, under these circumstances, split up at once into carbonic acid and a substitution acid of comenic acid. Accordingly bromine-water was poured upon powdered meconic acid; lively effervescence took place, which was found to result from the evolution of carbonic acid, and complete solution subsequently ensued. The fluid, when left at rest a considerable time, deposited a few long prismatic crystals of great beauty; a much more copious product was obtained by gentle evaporation. Recrystallization from hot water gave groups of brilliant square prismatic crystals, of which 6·787 grs., dried at 212°, gave, when burnt with lime, 5·480 grs. bromide of silver. This experiment gives a per-centage of 34·36 bromine; 34·04 is that corresponding to the formula of dry bromocomenic acid:—$2HO, C^{12} \left\{ \begin{matrix} H \\ Br \end{matrix} \right\} O^8$. The nature of the reaction is seen in the equation—

$$C^{14} H^4 O^{14} + 2Br = C^{12} \left\{ \begin{matrix} H^3 \\ Br \end{matrix} \right\} O^{10} + HBr + 2CO^2.$$

Crystals of oxalic acid were obtained by evaporating the original mother-liquors to a small bulk.

Æthers of Meconic Acid.

When absolute alcohol is poured upon meconic acid, and the mixture is agitated, partial solution takes place, accompanied by a considerable fall in temperature, amounting to about 10° or 12° F.; application of a gentle heat causes complete solution. A stream of hydrochloric acid gas passed through the fluid is attended by the usual result observed in these cases, the formation of an æther compound; but in this instance more than one of such substances are produced, and the relative proportion of the individual products depends on the amount of acid gas and the strength of the alcohol employed; I say the strength of the alcohol, because rectified spirit serves to produce ætherification, and I have employed it, but have found it disadvantageous, because whenever I did so I observed the formation of an uncrystalline compound, which very much impeded the purification of the other substances. The large amount of water of crystallization of meconic acid, amounting to fully 25 per

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cent., tends to dilute the alcohol; and I have sometimes dried the acid at 212° F. before using it, and found this a good plan when working with rectified spirit.

The results I have observed may be stated in a few words as preface to the description of the individual products. When a current of dry hydrochloric acid gas is passed through an alcoholic solution of meconic acid till it fumes strongly, and the fluid is set aside to cool, there appears, after a shorter or longer time, according to the circumstances above referred to, a deposit in feathery crystals. The fluid filtered from this, where absolute alcohol has been used, gives no further deposit; but, in the case of rectified spirit, another less crystalline substance appears after some little time. On evaporating the liquid, which has ceased to give deposits, to complete dryness, the chief constituent of the residue is found to be a substance fusing under boiling water; it is more or less accompanied by the other bodies according to the said conditions.

Æthylomeconic Acid.—The first deposit I have usually found to be so nearly a pure and uniform substance, that one recrystallization from hot water, after a little washing, was sufficient to render it completely so; it then appeared as highly crystalline in brilliant short needles. The following is its analysis:—

Carbon.....	47·39	47·12	18 =	108	47·36
Hydrogen	3·75	3·66	8	8	3·50
Oxygen	..	..	14	112	49·14

from which it is obvious that we have here an acid æther, analogous to phosphovinic acid, in which 1 atom of water of a tribasic acid is replaced by an equivalent of æther; its rational formula is therefore $2HO, C^4 H^5 O C^{14} HO^{11}$, according to which it is a bibasic acid; this I shall presently show to be the case. I propose to call this the æthylomeconic acid, in preference to meconovinic acid, both as more expressive of one of its constituents, and to facilitate its comparison with another æther, to be described shortly, which I should hardly know how to name otherwise than by calling biethylomeconic acid, containing, as it does, 2 equivs. of æther.

Æthylomeconic acid, when pure, crystallizes from boiling water in brilliant small crystals, which, when magnified, are seen to be square prismatic needles. It is very readily soluble in this menstruum, also in æther and common alcohol when warmed, less soluble in absolute alcohol. It separates from concentrated solutions in these three fluids in groups of stellate crystals, and when they are left to spontaneous evaporation, in long needles. It is anhydrous; its crystals lose no weight either *in vacuo* or at 212° F. It fuses at about 316°–318° F. to a transparent yellowish liquid, with the formation of a sublimate in very brilliant rhombic crystals.

Its aqueous solution reacts strongly acid, and readily coagulates the white of eggs. It imparts to persalts of iron a deep red colour. It decomposes carbonates with effervescence.

It is bibasic, forming two series of salts; the acid ones are readily crystallizable. Its salts are very stable, the acid being recoverable from them by decomposition with stronger acids.

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Acid Æthylomeconate of Baryta.—When carbonate of baryta is added in successive small quantities to water covering solid æthylomeconic acid, lively effervescence ensues, and the acid quickly disappears; there is formed at the same time a small amount of an insoluble yellow salt. If the fluid be filtered immediately on the cessation of the effervescence, and the vessel be placed under the receiver of an air-pump and a vacuum made, a considerable deposit of carbonate of lime, which had been held in solution by the carbonic acid now liberated, takes place. By a second filtration, a clear yellowish fluid is obtained, which yields, on evaporation *in vacuo* or at a gentle heat, very well-defined brilliant rhombic crystals of a yellow colour. A specimen prepared in this way, and dried at 212°, gave the following results:—

Carbon	36·20	18 =	108	36·53
Hydrogen	2·63	7	7	2·36
Oxygen	..	13	104	35·19
Baryta	26·17	1	76·64	25·92

which lead to the formula, for the dried æthylomeconate of baryta, of BaO, HO, $C^4 H^5 O C^{14} HO^{11}$. The crystals contain water, which they lose on drying; but I missed ascertaining the quantity.

Acid Æthylomeconate of Silver.—I obtained this salt by adding an aqueous solution of the former to nitrate of silver; a precipitate was immediately formed, which, upon resolution in boiling water, after washing, crystallized out on cooling of the fluid in groups of fine small stellate crystals, brilliant and white. This salt is remarkably stable, remaining perfectly unchanged in appearance when exposed a long time to the diffused daylight of summer. It gave the following results on analysis:—

Carbon	31·92	18 =	108	32·22
Hydrogen.....	2·20	7	7	2·08
Oxygen.....	..	14	112	33·45
Silver	31·94	1	108·1	32·25

which lead to the formula AgO, HO, $C^4 H^5 O C^{14} HO^{11}$ for the dried salt; the crystals contain 5·24 per cent. or 2 equivs. of water, which are expelled at 212°. The formula AgO, HO, $C^{18} H^6 O^{12} + 2Aq$ requires 5·08. An aqueous solution of acid æthylomeconate of baryta gives with acetate of lead a yellowish-white, with sulphate of copper a pale green, and with perchloride of iron a red-brown precipitate; this last is readily soluble in an excess of the iron salt, forming with it a dark red fluid.

Neutral Salts of Æthylomeconic Acid.—I have not been successful in procuring these salts absolutely pure, although I have tried many. On one occasion I obtained, by saturating æthylomeconic acid as nearly as possible with carbonate of baryta at a temperature of 212°, and subsequent filtering of the fluid, a salt which deposited on cooling in small short yellow needles, and which furnished, after being dried at 212°, 41·89 per cent. of baryta; the formula 2BaO, $C^4 H^5 O C^{14} HO^{11}$ requires 42·19.

Although this result is satisfactory, I could not succeed, upon

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repetition of the experiment, in obtaining an analytical number sufficiently close to confirm it. Those I obtained by heating æthylomeconic acid with excess of carbonate of baryta varied from 42 to 44·5 per cent. baryta, which lead to the conclusion that the acid forms basic combinations in addition to acid and neutral salts. The other alkaline earths showed similar deportment with the acid; and when it is heated with an excess of carbonate of silver, it remains almost entirely undissolved in some basic combination.

When æthylomeconic acid is heated with an excess of caustic potash or soda, meconates of these bases are produced. An excess of caustic ammonia decomposes it very readily.

[To be continued.]

On Stanæthyle, a new Organic Radical containing Tin.
By A. CAHOURS *and* A. RICHE.

The beautiful researches of Dr. Frankland on the isolation of the alcoholic radicals have shown, that, by causing metallic zinc to act upon the hydriodic æthers at a temperature of 302° F., there are obtained, besides the pretended radicals of the alcohols, combinations of zinc with different carburets of hydrogen, which present the composition of methyle, æthyle and amyle. In concluding his remarkable memoir, Dr. Frankland observes, that arsenic, tin, and potassium readily effect the decomposition of hydriodic æther; whilst iron, lead, mercury, and copper do not cause any sensible decomposition, at all events within the limits of 302° and 392°.

It is therefore probable, that by acting with the different metals upon the hydriodic æthers, we should in several cases obtain results presenting a more or less close analogy with those offered by zinc. Nothing having been published on this subject for the last three years, I undertook, with the assistance of one of my former pupils, M. Riche, some researches relative to the action of some metals upon the hydriodic æthers. The following are the results we have obtained with tin:—

When tin-filings are heated with hydriodic æther in sealed tubes to a temperature of 320°–356° in an oil-bath, the liquid is seen gradually to diminish, and in the course of from twenty to twenty-four hours the mass solidifies on cooling into a substance consisting of large crystals. This solid product is a mixture of unaltered tin-filings, of the yellow and red iodides of tin, and of a substance crystallizing in colourless needles, which dissolves in water, and still more readily in alcohol, by which it can be separated from the other products. By treating the solid mass taken from several tubes with strong alcohol, filtering the liquid, and leaving it to spontaneous evaporation, very brilliant long needles separate, which possess a very marked odour of radish, and the yellowish colour of which is owing to the decomposition of a small quantity of the substance, a result which occurs especially when the vessel containing the solution is exposed to the rays of the sun. By pressure between blot-

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ting-paper, the crystals become colourless, and almost completely lose their odour.

Thus purified, this substance melts at 100° F. into a very limpid oil; at a higher temperature it gives off colourless vapours, which are deposited on the sides of the vessel in which the distillation is carried on in long colourless needles. Only a minute trace of the substance is decomposed. In cold water it dissolves sparingly. When heated, it melts and falls to the bottom of the water as a colourless oil, which gradually dissolves. It dissolves readily in alcohol, especially hot, and still more so in anhydrous æther. On analysis, this compound furnished the following results:—

Carbon.....	10·98	11·02	11·09	11·17	4=	24	11·21
Hydrogen	2·52	2·57	2·44	2·43	5	5	2·32
Tin	..	..	..	..	1	59	27·57
Iodine	58·10	58·34	..	..	1	126	58·80

The solution of this compound behaves with metallic solutions precisely like the soluble iodides; it produces with salts of lead, mercury, and silver the same precipitates as the iodide of potassium.

When a solution of nitrate of silver is gradually added to a solution of the preceding compound, a precipitate of iodide of silver is obtained, and the filtered liquid deposits on evaporation a white crystalline compound, the analysis of which led to the formula $NO^5, C^4 H^5 SnO$.

The sulphate of silver, treated in the same manner, gave a salt in minute nacreous scales, the composition of which is expressed by the formula $SO^3, C^4 H^5 SnO$.

On adding ammonia to a solution of the preceding salts, a heavy white amorphous precipitate separates, which dissolves readily in dilute nitric and sulphuric acids, again furnishing the above salts. With acetic acid it forms a crystalline compound; it likewise dissolves in hydrochloric acid, and gives on evaporation a compound which crystallizes in white needles of great beauty, with the formula $C^4 H^5 SnCl$. The amorphous precipitate formed by ammonia is represented by the formula $C^4 H^5 SnO$.

The examination of these different compounds leads us to admit the existence of a ternary group, $C^4 H^5 Sn$, which behaves like a true radical analogous to cacodyle and stibæthyle, and to which we therefore give the name of *stanæthyle*.

Iodide of methyle under the same circumstances furnishes analogous results; the corresponding compound, *stanmethyle*, $C^2 H^3 SnI$, is obtained; but the experiment does not succeed so well. Iodide of amyle, treated in the same manner, experiences no perceptible alteration, even after a contact of ten or twelve days.

If we admit with M. Regnault that the simple æthers are all derived from a carburet of hydrogen, $C^4 H^6$, by the substitution of an equivalent of oxygen, chlorine, iodine, or sulphur for an equivalent of hydrogen, these bodies enter as an integrant molecule of the compound—a result which is in perfect accordance with the passive action of these compounds in the presence of the reagents for chlorine,

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iodine and sulphur. We must consider the compound $C^4 H^5 Sn$ as corresponding to hydrochloric æther, Sn replacing Cl. But as tin has far more electro-positive properties than the hydrogen which it replaces in the compound $C^4 H^6$, we can understand why the æthylide of tin behaves like a true radical.—*Comptes Rendus*, July 19, 1852.

On the Presence of Fluorine in the Stems of Gramineæ, Equisetaceæ, and other Plants, with some Observations on the Sources from which Vegetables derive this Element. By GEORGE WILSON, M.D.

The author commenced by stating, that the earliest observer of the presence of fluorine in plants was Will of Giessen, who found traces of it in barley, the straw and grain of which were analysed together. The author reported to the Botanical Society, some four years ago, the results of his earlier researches into the distribution of this element throughout the vegetable kingdom, which were not very numerous or very encouraging. One reason of this was the small extent to which fluorine occurs in plants; another, and practically as serious a reason, was the difficulty of separating and recognising fluorine when accompanied by silica. The presence of this body in a plant, besides greatly complicating the investigation, rendered the employment of platina vessels essential, and thus limited the amount of material which could be subjected to examination, besides making it difficult or impossible to observe the progress of an analysis.

The author then stated, that, in the course of some recent investigations into the presence of fluorine in siliceous rocks, he had succeeded in devising a process which was also applicable to plants, and could be carried on in the ordinary glass vessels of the laboratory. The process in the case of plants was as follows:—The plant under examination was burned to ashes as completely as possible. The ashes were then mixed in the cold with oil of vitriol, so as to secure the decomposition of the salts of volatile acids present. The mixture was then transferred to a retort, or flask, provided with a bent tube dipping into water, and the liquid raised to the boiling-point, when fluorine, if present, was evolved in combination with the silicon of the silica, as the gaseous fluoride of silicon, which dissolved in the water with separation of some gelatinous silica. The resulting solution was neutralized with ammonia and evaporated to complete dryness, when the whole of the silicon passed into the condition of insoluble silica, and water dissolved the fluoride of ammonium. The solution of this fluoride could then be dried up and moistened with sulphuric acid, when hydrofluoric acid was evolved, which might be made permanently to record its presence by causing it to etch glass in the usual way. The author has in the meanwhile applied this process almost solely to the stems and trunks of plants, especially to those containing silica, reserving for subsequent investigation their other organs, especially their seeds and fruits. The following were the results obtained:—

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Table of Plants examined for Fluorine. The numbers represent grains of ashes, except in the case of Tabasheer and Wood Opal. The blanks imply that the weight was not known:—

Ashes in grains.	Name of plant.	
200	*Equisetum limosum*	Distinct etching.
	Bambusa arundinacea	Ditto.
	Charcoal (derived chiefly from Oak, and to a smaller extent from Birch)	Ditto.
	Coal	Ditto.
	Barley straw.....	Ditto.
	Hay (Ryegrass)	Ditto.
35	*Equisetum variegatum*	Faint etching.
19	——— *hyemale*	Ditto.
255	——— *palustre*	Ditto.
	Dactylis cæspitosa	Ditto.
99	*Elymus arenarius*.....	Ditto.
495	*Saccharum officinarum*.....	Ditto.
1040	African Teak	Ditto.
	Smilax latifolia	No etching.
	Rosmarinus officinalis	Ditto.
235	*Bambusa Nepalensis*	Ditto.
	Polypodium vulgare.....	Ditto.
537	Tree Fern.....	Ditto.
24	*Phalaris arundinacea*	Ditto.
240	Malacca Cane	Ditto.
50	Cocoa-nut shell.....	Ditto.
127	*Tectona grandis*	Ditto.
80	Tabasheer	Ditto.
1680	Wood Opal	Ditto.

On this table the author remarked, that the siliceous stems which he had found to abound most in fluorine, were exactly those which contained most silica. In particular, deep etchings were procured from the Equisetaceæ and from the Gramineæ, especially the common Bamboo. The last was known to contain silica in such abundance that it collected within the joints in white masses, nearly pure, and had long, under the name of Tabasheer, been an object of interest to natural philosophers. The horse-tails were scarcely less remarkable for the amount of silica contained in their stems, which had led to the employment of one of them (*Equisetum hyemale*) in polishing wood and metals. The African Teak, which like the Bamboo is known sometimes to secrete silica, was also found to contain fluorine, though much less largely than the plants named; whilst the strongly siliceous stems of Barley and Ryegrass also yielded the element in marked quantity. The Sugar-cane, however, gave less striking results than might have been expected, and the same remark applied to the Malacca-cane. Two specimens of silicified wood and one of Tabasheer gave no evidence of the presence of fluorine. So far, however, as the plants named in the preceding table are concerned, the author does not wish it to be inferred from the negative results which are detailed,

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that the plants in question are totally devoid of fluorine. With larger quantities of their ashes, positive results would, in all probability, be obtained.

The author's general conclusions were as follows:—1st, that fluorine occurs in a large number of plants; 2nd, that it occurs in marked quantity in the siliceous stems of the Gramineæ and Equisetaceæ; 3rd, that the quantity present is in all cases very small; for although exact quantitative results were not obtained, it is well known that a fraction of a grain of fluoride will yield with oil of vitriol a quantity of hydrofluoric acid sufficient to etch glass deeply, so that the proportion of fluorine present, even in the plant-ashes which contain it most abundantly, does not probably amount to more than a fraction per cent. of their weight. The proportion of fluorine appears to be variable, for different specimens of the same plant did not yield concordant results.

In this, however, there is nothing anomalous, for some Bamboos yield *Tabasheer* largely, whilst others are found to contain none. It seems not unlikely that soluble fluorides ascending the siliceous stem of a plant, on their way to the seeds or fruits in which they finally accumulate, may be arrested by the silica, and converted into insoluble fluosilicates (fluorides of silicon and of a metal); and a Bamboo, for example, secreting Tabasheer, may effect this change where one less rich in silica cannot determine it. The slow or quick drying of a stem may also affect the fixation of fluorides in the stems or trunks of plants.

The sources of the fluorine found in plants may be regarded as preeminently two,—1st, simple fluorides, such as that of calcium, which are soluble in water, and through this medium are carried into the tissues of plants; and 2nd, compounds of fluorides with other salts, of which the most important is probably the combination of phosphate of lime with fluoride of calcium. This occurs in the mineral kingdom in apatite and phosphorite, and in the animal kingdom in bones, shells and corals, as well as in blood, milk, and other fluids.

A recent discovery of the author's, communicated to the Royal Society of Edinburgh, has shown that fluorides are much more widely distributed than is generally imagined, and that the trap rocks near Edinburgh, and in the neighbourhood of the Clyde, as well as the granites of Aberdeenshire, and the ashes of coal, contain fluorides, so that the soils resulting from the disintegration of those rocks cannot fail to possess fluorides also. All plants accordingly may be expected to exhibit evidence of their presence in the following portions of their tissues or fluids:—

1. In the ascending sap, simple fluorides.

2. In the descending sap, in association with the albuminous vegetable principles, and in the seeds or fruits, in a similar state of association, fluorides along with phosphates.

3. In the stems, especially when siliceous and hardened, fluorides in combination with silica. The investigation is still in progress.—*Proceedings of the Botanical Society of Edinburgh*, July 8, 1852.

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On two new Acids resulting from some Reactions of Nitrotartaric Acid. By M. DESSAIGNES.

The following two new acids were discovered while making some experiments for the purpose of studying the action of a mixture of nitric and sulphuric acids upon various organic acids.

Tartaric acid in very fine powder is quickly dissolved in 4½ parts of monohydrated nitric acid, and an equal volume of sulphuric acid added to the solution. On agitation, the whole solidifies into a white paste. The mixture is freed from the greater portion of the sulphuric acid which it contains by leaving it for a day or two under a bell-glass between two porous tiles. It then forms a soft, white, silky mass, which on exposure to the air gives off copious white fumes. It is purified by dissolving it in lukewarm water, and immediately cooling the solution in water to 32° F. The liquid congeals to a mass of interlaced silky crystals, which, on being broken up upon a filter, decreases considerably in bulk, while giving off a large quantity of mother-liquor. The crystals are then pressed between folds of blotting-paper. This acid is very readily decomposed. Although I have not yet analysed it, the examination of its products of metamorphosis has convinced me that it is nitrotartaric acid.

In fact, when saturated with ammonia, and then heated after the addition of hydrosulphate of ammonia, it is decomposed with effervescence, and a copious deposit of sulphur; the filtered solution yields on evaporation crystals of the neutral tartrate of ammonia. Further, the crude acid, as obtained after pressure between the two porous tiles, on being exposed to the air, diffuses for several days white vapours of nitric acid, and is converted into a heavy crystalline substance, which yields on resolution large crystals of tartaric acid free from nitric acid.

Nitrotartaric acid, on the other hand, dissolved in water and left to spontaneous decomposition, or treated with a current of sulphureted hydrogen, or better still combined with potash or oxide of lead, experiences a totally different metamorphosis, and furnishes, among other products, an acid, the composition and properties of which prove it to be distinct from all the hitherto-known organic acids.

I shall merely describe in this place the preparation of this acid by the spontaneous decomposition of an aqueous solution of nitrotartaric acid. This solution gives off bubbles of gas even at a few degrees above 32°. The disengagement gradually increases, and the liquid assumes a faint blue tint. The gas is then composed of $\frac{5}{6}$ deutoxide of nitrogen and $\frac{1}{6}$ carbonic acid. After several days there is no further production of gas. If the liquid be then heated to 104°–122° F., a lively effervescence, resulting from the escape of pure carbonic acid, ensues; and on now concentrating the liquid almost the sole product is oxalic acid. On the other hand, if the liquid, which no longer disengaged any gas in the cold, is placed in a chamber heated scarcely to 86°, it again begins to give off a few bubbles when concentrated, and finally yields crystals of a new

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acid, sometimes, but not always, accompanied by a small quantity of oxalic acid. The amount of the new product is far less in weight than that of the crystals of tartaric acid employed for its preparation.

It forms tolerably large prisms, which sometimes remain transparent in the air, sometimes become semi-opake, and as it were fibrous; these latter do not part with any water at 212°. Heated in an oil-bath, they melt at about 347°, giving off gas and a little water, and leaving a slightly-coloured amorphous residue nearly insoluble in water. When distilled rapidly over a lamp, the new acid furnishes another acid, which is very soluble, crystalline, and scarcely volatile.

The new acid dissolved in water is not altered by boiling. It does not precipitate the chlorides of calcium and barium, the acetate of potash, the sulphates of magnesia and copper, or the perchloride of iron, even when an excess of ammonia is present; it furnishes precipitates with the nitrates of lead and silver, the protonitrate of mercury, and the perchloride of mercury. All these precipitates are heavy and crystalline. It also precipitates the acetates of baryta, copper and lime. The latter precipitate dissolves in chloride of ammonium.

The neutral salt of ammonia furnishes precipitates with the chlorides of calcium, barium and platinum.

Two combustions of the acid, dried *in vacuo*, with oxide of copper and chlorate of potash, and three analyses of the silver salt dried *in vacuo* (it is decomposed at 212°), furnished—

	Acid.				Silver salt.			
Carbon	30·00	30·41	3	=30·00	10·74	..	3	=10·77
Hydrogen ..	3·38	3·64	4	3·33	0·70	..	2	0·60
Oxygen	..	..	5	66·67	..	..	5	23·96
Silver	..	..		..	64·37	64·70	1	64·67

If we suppose this acid to be bibasic (and I may state that it forms an acid salt with ammonia, crystallizing in beautiful prisms), its formula would become $C^6 H^8 O^{10}$, so that it would be a homologue of malic acid, $C^8 H^{12} O^{10}$. But to establish this remarkable homology, malic acid at present being the only one of its series, it must be shown that the acid described is bibasic, and further, that its principal reactions exhibit a decided analogy with those of malic acid. This I am at present investigating. It will also be interesting to study the two acids derived from tartaric acid with reference to their action on polarized light.—*Comptes Rendus*, xxxiv. p. 731.

On Platinum-Black and the Compound of Æthyle and Mercury of Sobrero *and* Selmi. *By* Dr. W. Knop.

That platinum-black frequently contains an organic substance is sufficiently evident from the facts already known regarding it. Gmelin has put the question in his 'Lehrbuch,' p. 722:—"Is the hissing produced by some kinds of platinum-black on being heated, owing to the presence of some carbonaceous compound?" From Gerhardt's discovery of a compound of mercury with æthyle, it ap-

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peared probable that there might also exist a compound of platinum and æthyle. The following experiment will perhaps be considered decisive. Pieces of potassium or sodium were added to an alcoholic solution of chloride of platinum. An extremely fine platinum-black, which subsided with difficulty, was obtained, which, like that of Descotils, flashed like gunpowder when moderately heated, and scintillated strongly when thrown into a flame. It is gradually decomposed in drying, and on this account, as well as from its explosive nature, could not be analysed; but in the course of eight or ten days, or more, especially when exposed to the sunlight moistened with water, it emits a distinct odour of acetic acid, and is without doubt a compound of æthyle and platinum.

As Werther and Brückner, in repeating the experiments of Sobrero and Selmi, did not obtain the compound of mercury with a substance belonging to the æthyle series, which these chemists stated they had procured, a solution of chloride of mercury was treated in the same manner as above in absolute alcohol. The product was an oxychloride of mercury, containing chloride of potassium.—*Pharm. Central Blatt.*, xxiii. p. 431.

On the Constitution of Citric Acid. By L. Pebal.

The author, after giving a general summary of the literature of the subject, states that he selected for investigation the anilides of citric acid in the hope of deciding as to the constitution of citric acid.

Pulverized crystals of citric acid were treated with a small excess of hydrated aniline in an oil-bath at 284°–302° F. until the mass showed scarcely any bubbles. The residue formed a brownish-red vitreous mass; it was exhausted with boiling water, which removed the *citromonanilic acid* described further on. The residue from this treatment was dried and rubbed to a powder; it was of a yellow colour, and dissolved in alcohol. From this solution three different substances were obtained by crystallization,—*citronanilide* in prisms, *citrobianile* in six-sided tables, and a third body apparently of the same constitution as the latter.

Citronanilide, $C^{48}\,H^{23}\,N^{3}\,O^{8}$, is very sparingly soluble or almost insoluble in water; slightly soluble in boiling alcohol, from which it separates on spontaneous evaporation in thin colourless prisms truncated at right angles. Sometimes they are very minute, generally arranged in concentric groups, with longitudinal striæ and a mother-of-pearl lustre. Their solution has no action on vegetable colours. When boiled with caustic potash of 1·27 spec. grav. or concentrated solution of ammonia, they are apparently not altered, and can be thus freed from adherent six-sided tablets of citrobianile. The air-dried crystals lose nothing in weight over sulphuric acid. Analysis furnished—

Carbon	69·08	69·00	69·01	69·17	69·14	48	= 288	69·06
Hydrogen	5·72	5·65	5·65	5·62	5·57	23	23	5·52
Nitrogen	..	10·43	..	..	..	3	42	10·07
Oxygen	..	..	..	..	..	8	64	15·35

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This substance may be regarded as tribasic citrate of aniline minus 6 equivs. of water:—

$$\left.\begin{matrix} C^{12}\,H^{7}\,N\,HO \\ C^{12}\,H^{7}\,N\,HO \\ C^{12}\,H^{7}\,N\,HO \end{matrix}\right\} C^{12}\,H^{5}\,O^{11} - 6HO = C^{48}\,H^{23}\,N^{3}\,O^{8}.$$

Citrobianile, $C^{36}\,H^{16}\,N^{2}\,O^{8}$, separates with the preceding substance from the alcoholic solution. For its preparation the author advises the employment of aniline and citric acid in the proportion requisite for the formation of a bibasic salt. The solution of the perfectly pure substance in alcohol does not change the colour of blue litmus-paper, and deposits on spontaneous evaporation colourless six-sided plates, which are transparent, very sparingly soluble in water, readily soluble in boiling alcohol, and are converted, by long treatment with a strong boiling solution of ammonia, into the corresponding anilic acid. The air-dried crystals experience no loss in weight over sulphuric acid. They gave on analysis—

Carbon	66·51	36 =	216	66·66
Hydrogen.....	5·04	16	16	4·94
Nitrogen	..	2	28	8·64
Oxygen.....	..	8	64	19·76

It may be admitted that citrobianile is formed from the bibasic citrate of aniline by the elimination of 6 equivs. water:—

$$\left.\begin{matrix} C^{12}\,H^{7}\,N\,HO \\ C^{12}\,H^{7}\,N\,HO \\ HO \end{matrix}\right\} C^{12}\,H^{5}\,O^{11} - 6HO = C^{36}\,H^{16}\,N^{2}\,O^{8}.$$

The *third substance* crystallized in prisms, which were readily distinguished from those of citronanilide by their becoming dull and opake over sulphuric acid. The crystals are oblique truncated, four-sided needles; at 212° they lost about 1·08 per cent. of their weight in the air-dried state. The substance, dried at 212°, furnished 66·71 per cent. of carbon and 5·0 per cent. of hydrogen. The composition agrees exactly with that of citrobianile.

Citrobianilic Acid, $C^{36}\,H^{18}\,N^{2}\,O^{10}$, is obtained by boiling citrobianile with a concentrated solution of ammonia. The solution, on being mixed with hydrochloric acid, deposits the hydrated acid as a gaseous precipitate. From the filtered liquid a further quantity of the acid separates in small warty crystals. From the alcoholic solution of the washed precipitate, which turns blue litmus-paper red, the acid separates in soft, concentric groups of silky needles, which dissolve readily in alcohol, sparingly in water. The acid melts at about 307°, and is converted with loss of water into the anile. The melted residue, dissolved in alcohol, furnished the latter in six-sided prisms. The acid gave on analysis—

Carbon	63·07	36 =	216	63·16
Hydrogen.....	5·41	18	18	5·26
Nitrogen	..	2	28	8·19
Oxygen.....	..	10	80	23·39

According to this, citrobianilic acid is formed from citrobianile by

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the assimilation of 2 equivs. of water, $C^{36} H^{16} N^2 O^8 + 2HO = C^{36} H^{18} N^2 O^{10}$, and may be viewed as bibasic citrate of aniline minus 4 equivs. of water:—

$$\left.\begin{matrix} C^{12} H^7 N\, HO \\ C^{12} H^7 N\, HO \\ HO \end{matrix}\right\} C^{12} H^5 O^{11} - 4HO = C^{36} H^{18} N^2 O^{10}.$$

Citrobianilate of Silver, $C^{36} H^{17} N^2 O^{10} Ag$, falls as a white precipitate when a neutral solution of the acid in dilute ammonia is mixed with nitrate of silver; washed with cold water, pressed between blotting-paper, and dried over sulphuric acid, it furnished on analysis—

Carbon	47·81	36 =	216·0	48·10
Hydrogen	3·87	17	17·0	3·78
Nitrogen.....	..	2	28·0	6·23
Oxygen	..	10	80·0	17·82
Silver.....	24·01	1	108·1	24·07

Citrobianilate of Baryta, $BaO, C^{36} H^{17} N^2 O^9$, is obtained by precipitating a neutral solution of the acid in ammonia with chloride of barium. It contained 18·48 per cent. of baryta; the formula requires 18·68.

Citrobianilate of Aniline, $C^{12} H^7 N, HO + C^{36} H^{17} N^2 O^9$, is obtained by digesting citrobianilic acid with hydrated aniline. On evaporating the solution, the salt crystallized in colourless transparent laminæ, which experienced a very slight loss in weight over sulphuric acid. Analysis gave—

Carbon	66·18	48 =	288	66·21
Hydrogen.....	5·89	25	25	5·75
Nitrogen	..	3	42	9·65
Oxygen.....	..	10	80	18·39

Citrobianilic acid is consequently a monobasic acid, and its formula $HO, C^{36} H^{17} N^2 O^9$.

Monobasic Citrate of Aniline, $C^{12} H^7 N, \begin{matrix} HO \\ HO, \\ HO \end{matrix} C^{12} H^5 O^{11}$, is obtained by evaporating to dryness over sulphuric acid an alcoholic solution of citric acid with an equivalent amount of aniline which contains a little water. A brownish-red mass is obtained, in which crystals form only after some time, but at length the entire mass becomes crystalline. It is then broken up in a mortar with the addition of a little alcohol, the liquid pressed through linen, and the mass crystallized from strong alcohol over sulphuric acid. The salt consists of groups of slender needles, which melt somewhat below 212°, are readily soluble in alcohol, and still more so in water. The substance, dried over sulphuric acid, furnished—

Carbon.....	50·41	50·81	24 =	144	50·53
Hydrogen	..	5·46	15	15	5·26
Nitrogen	..	..	1	14	4·91
Oxygen	..	..	14	112	39·30

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Monobasic Citromonanilic Acid, $C^{24}H^{11}NO^{10}$.—When the preceding salt is kept at a temperature between 284°–302°, it solidifies, after water has escaped, in part even at the high temperature, and in part on cooling, into a crystalline substance, which dissolves very readily in water if an excess of aniline was avoided, and separates on spontaneous evaporation in crystalline granules, but more frequently in the form of verrucous crusts, made up of little prisms. They can be obtained colourless by treating their solution in water with animal charcoal, and recrystallization. They readily dissolve in alcohol; the solution turns blue litmus-paper red. The substance, dried over sulphuric acid, furnished on analysis:—

Carbon	57·66	57·65	57·83	24 =	144	57·83
Hydrogen ..	4·55	4·61	4·58	11	11	4·42
Nitrogen....	..	..	..	1	14	5·62
Oxygen	..	..	..	10	80	32·13

If we deduct 4 equivs. water from the composition of the monobasic citrate of aniline, we obtain the above formula:—

$$\left.\begin{matrix} C^{12}H^{7}N\,HO \\ HO \\ HO \end{matrix}\right\} C^{12}H^{5}O^{11} - 4HO = C^{24}H^{11}NO^{10}.$$

Silver Salt, $AgO, C^{24}H^{10}NO^{9}$.—The solution of the acid in alcohol neutralized with ammonia furnished a white precipitate with an aqueous solution of nitrate of silver. The filtered solution deposited after some time crystalline granules, which were mixed with a small quantity of a pulverulent substance. After the latter had been removed by agitation and decantation, the granules were reduced to powder, dried over sulphuric acid, and analysed. The following numbers were obtained:—

Carbon	39·97	24 = 144·0		40·43
Hydrogen	2·86	10	10·0	2·81
Nitrogen	..	1	14·0	3·93
Oxygen	..	10	80·0	22·47
Silver.....	30·93	1	108·1	30·36

Aniline Salt, $C^{12}H^{8}NO, C^{24}H^{10}NO^{9}$.—The aqueous solution of the acid was saturated with aniline, and the coloured crystals obtained purified with animal charcoal. The salt crystallized from water in the form of granular masses, which are very readily dissolved by alcohol. The crystals, dried over sulphuric acid, lost a little hygroscopic moisture, and furnished on analysis—

Carbon.....	62·93	63·18	36 = 216		63·16
Hydrogen	5·36	5·33	18	18	5·26
Nitrogen	..	..	2	28	8·19
Oxygen	..	..	10	80	23·39

The analyses of the compounds hitherto described show that the acid is monobasic, and is represented by the formula $HO, C^{24}H^{10}NO^{9}$.

Silver Salt of the Bibasic Citromonanilic Acid, $2AgO, C^{24}H^{7}NO^{10}$.

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—When the aqueous solution of the bibasic citromonanilic acid is saturated with ammonia, and then mixed with nitrate of silver, a white caseous precipitate is formed. Washed with cold water and dried over sulphuric acid, it furnished on analysis—

Carbon	30·17	..	24 =	144·0	29·92
Hydrogen.....	2·41	..	11	11·0	2·29
Nitrogen	..	..	1	14·0	2·91
Oxygen.....	..	..	12	96·0	19·95
Silver	44·57	44·74	2	216·2	44·93

It was found impossible to obtain the hydrate of the acid, 2HO, $C^{24} H^{11} NO^{10}$. The silver salt, on being decomposed in cold water with dilute hydrochloric acid, furnished, on the spontaneous evaporation of the solution, small distinct prisms of a yellowish colour, but only the monobasic citromonanilic acid could be obtained. The stability therefore of the compound 2HO, $C^{24} H^{11} NO^{10}$ must be exceedingly feeble, as even under these circumstances an equivalent of water is formed from the anhydrous acid, $C^{24} H^{11} NO^{10}$.—Liebig's *Annalen*, lxxxii. p. 86.

General Remarks upon the Behaviour of Water towards Carbonic Acid in Carbonates. By H. Rose.

Investigations on the influence of water in chemical decompositions have shown that water can expel a certain quantity of carbonic acid from the carbonates of most oxides, the carbonic acid being replaced by water. The quantity of carbonic acid expelled is different in different carbonates, and is regulated according to the affinity of the undecomposed carbonate for the resulting hydrate. They combine apparently in most cases in a definite simple proportion, which however varies with the different metallic oxides.

The affinity which water exhibits for the base when it expels the acid, appears in many cases to be nearly as great as that possessed by the carbonic acid; for the very same bases which retain water with the greatest pertinacity at the highest temperatures, unite also with carbonic acid with so close an affinity that it cannot be expelled from them at the same high temperatures. These bases are potash, soda, baryta, strontia and lime. The latter, as is well known, loses both its carbonic acid and water at a red heat.

At various temperatures, however, the affinity of these bases for water is sometimes greater, sometimes less, than that exhibited for carbonic acid. If, as has been shown by Gay-Lussac and Thenard, the vapour of water be passed over carbonate of baryta, potash or soda, heated to redness, carbonic acid gas is immediately evolved. The water in this case acts by its mass; it expels the carbonic acid in order to combine with the bases which were united with it.

Under certain circumstances water exhibits even a stronger affinity for these bases than carbonic acid. The anhydrous alkaline earths, if they have not been exposed to too high a temperature, absorb water with great avidity, and become changed into hydrate with great evolution of heat; but if they be freed from all moisture,

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they absorb no carbonic acid at ordinary temperatures, and can only unite with it at an elevated temperature. Carbonic acid is only absorbed at ordinary temperatures by the alkaline earths in the presence of water. Even hydrate of potash, in the freshly-fused state, does not combine with carbonic acid, and only absorbs it when moistened with water. Hydrate of soda, on the contrary, in the freshly-fused state, can absorb dry carbonic acid gas, although very gradually. At an elevated temperature, however, the hydrates of potash and soda can combine with carbonic acid in the absence of water.

If water and carbonic acid expel each other from their combinations and act like acids, they are distinguished from one another in this respect, that although carbonic acid is one of the weakest acids, it never acts as a base even towards the strongest acids; whilst water, on the other hand, belongs to the oxides, which only act as acids towards strong bases, but when combined with strong acids must be regarded as bases. It is owing to this that carbonic acid does not form a chemical compound with water.

Nevertheless there are compounds in which carbonic acid may be considered as combined with water. These are the crystallized bicarbonates of potash and soda. It is well known that neither of these can be procured free from water in the solid state; and that, when the second atom of carbonic acid, which is only weakly held in these salts, is driven off at an elevated temperature, it disappears in company with the water. If carbonic acid be regarded as one of the so-called monobasic acids, the bicarbonates of the alkalies are acid salts; or they may be considered, like many acid salts, as neutral double salts, in which the acid is combined with two bases, of which water is one. A series of experiments has shown, however, that by a gradually elevated temperature carbonic acid and water are not equally volatilized from the bicarbonates of the alkalies, so that the water must be considered as water of crystallization.—*Bericht der Akad. der Wissensch. zu Berlin*, 1852, p. 209.

On the Conversion of Salicylic Acid into Monochlorinated Benzoic Acid. By L. Chiozza.

It is known from the observations of M. Cahours, that by placing the perchloride of phosphorus in contact with certain volatile organic acids, with 2 or 3 equivs. of oxygen, oxychloride of phosphorus, hydrochloric acid, and chlorides of the radicals of these organic acids, are obtained. This reaction is explained, in the case of benzoic acid, by the following equation:—

$$C^7 H^6 O^2 + PCl^5 = C^7 H^5 O, Cl + ClH + POCl^3.$$

Some experiments performed in M. Gerhardt's laboratory, with the view of obtaining the chloride of salicyle, have shown me that the action of perchloride of phosphorus with salicylic acid is not so well marked as with the acids studied by M. Cahours.

Leaving out of consideration the secondary products of the reaction, it may be represented in the same manner as for benzoic acid, with this difference, however, that the product does not split up im-

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mediately into hydrochloric acid and chloride of salicyle; and that this resolution, on being ultimately effected, gives, not chloride of salicyle, but a substance isomerous with it, monochlorinated benzoic acid.

On submitting the liquid obtained by the action of perchloride of phosphorus upon salicylic acid to distillation, it will be seen that the temperature rises rapidly; towards the end of the distillation the liquid puffs up, and leaves as a residue a very light charcoal.

By rectifying the product, and only collecting what passes between 392° F. and 482°, a highly refractive oily liquid is obtained, of a suffocating odour. This liquid is decomposed but slowly by cold water, but boiling water converts it immediately into hydrochloric acid and monochlorinated benzoic acid.

The difficulty of obtaining this oily substance in a state of purity has prevented me from analysing it; judging from its mode of decomposition, however, we may consider it as a hydrochlorate of monochlorinated benzoic acid, and assign to it the formula—

$$C^7 H^5 ClO^2, ClH.$$

I may remark here, that Mr. Stenhouse has already obtained monochlorinated benzoic acid, but mixed with the products of the more advanced action of chlorine on benzoic acid.

In a state of purity, monochlorinated benzoic acid forms beautiful, brilliant, acicular crystals, very like those of salicylic acid, from which it is easily distinguished by its not giving a violet colour to the persalts of iron. It differs also in all its properties from its isomer, the chloride of salicyle of M. Piria (hydruret of chlorosalicyle). It dissolves pretty readily in boiling water, from which it separates almost entirely on cooling. Its fusing-point is some degrees higher than that of benzoic acid. It sublimes without alteration.

Its analysis gave results agreeing with the formula $C^7 H^5 ClO^2$. The equivalent of monochlorinated benzoic acid has been established by the analysis of the silver salt, which contains $C^7 H^4 Ag ClO^2$.

This salt has the form of a crystalline precipitate. The baryta salt gave me results agreeing with the formula $C^7 H^4 Ba ClO^2$.—*Comptes Rendus*, May 31, 1852.

On the Occurrence of Propylamine. *By* M. Winckler.

By distilling ergotine with potash, the author obtained ammonia and propylamine. He supposes that this base is present as such in the ergotine, and that it is combined with formic acid in the grain.

By the distillation of train-oil soap with quick-lime and chloride of ammonium, he also procured propylamine.

By the distillation of fresh urine with lime, the author obtained a distillate which possessed the odour of propylamine. The liquid behaved with tincture of iodine like ammonia. By testing it with tannin and nitrate of silver, the presence of propylamine was shown. —Buchner's *Repert. f. Pharm.*, i. p. 162.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Composition of Spermaceti. By Dr. HEINTZ.

SPERMACETI has been considered by Chevreul to be a combination of æthal ($C^{32} H^{33} O + HO$) with margaric and oleic acids. Dumas and Stass afterwards showed, that by the action of hydrate of potash upon æthal at a temperature of 410°–428° F., the potash salt of an acid, which they called æthalic acid, was formed, with evolution of hydrogen gas. The composition of this acid is expressed by the formula $C^{32} H^{31} O^3 + HO$, and its melting-point is about 131° F. Shortly afterwards, Dr. L. Smith examined spermaceti, and believed that he had shown that it was nothing but a combination of this æthalic acid with æthal. The labours of M. Heintz show that the composition of spermaceti is much more complicated; that upon its saponification, æthal and a mixture of a whole series of acids are produced, but no æthalic acid; and that, in fact, æthalic acid, *i. e.* a chemically pure substance of the formula $C^{32} H^{31} O^3 + HO$, does not exist.

The method employed by M. Heintz for the investigation of spermaceti was shortly as follows:—1 part of solid dry caustic potash, free from carbonate of potash and other impurities, was dissolved in much alcohol, and the solution boiled with from 6 to 8 parts of commercially purified spermaceti until the latter was dissolved. In this manner the saponification was effected in a short time. The solution was precipitated with a concentrated watery solution of chloride of barium, and the liquid filtered whilst warm. The barytic precipitate was completely freed from æthal by hot alcohol. A first portion of baryta salts was thus obtained. The alcoholic solution furnished a second portion when the alcohol was distilled off and the residue extracted with æther. This baryta salt was not soluble in æther. A third small quantity was lastly procured by evaporating the ætherial solution, boiling the residue of æthal for a long time with muriatic acid, dissolving the fatty mass freed from baryta in alcohol, pressing the æthal which separated on cooling, and precipitating the residuary alcoholic solution with an alcoholic solution of acetate of baryta. The baryta salt thus obtained could be washed with cold alcohol.

The æthal, the alcoholic solution expressed from the last-mentioned baryta salt, and the three baryta salts themselves, had now to be investigated.

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The æthal, after being separated from a small quantity of unsaponified cetine, was found to agree with the composition given by Dumas, $C^{32} H^{33} O + HO$.

But in the alcoholic fluid which had been separated from the last-mentioned baryta salt, there was, together with a certain quantity of æthal, a peculiar substance, which was very readily fusible and soluble in alcohol in every proportion, but insoluble in water, and was scarcely free from æthal. This substance becomes fluid even at a temperature of 50°–54° F. It can only be freed from æthal by exposing the alcoholic solution to cold, and pressing the mass which separates in a solid state. This substance then remains in the solution, and can now be freed from any small quantities of fatty acids which may be present, by boiling with an alcoholic solution of potash, to which water is gradually added during the boiling. The analysis of this substance gave the formula $C^{18} H^{18} O^2$.

The fatty acids, which were procured from the three different baryta salts by boiling each separately with diluted muriatic acid, were investigated by the same method by which M. Heintz succeeded in ascertaining the true nature of human fat*.

Instead of acetate of lead, however, he employed acetate of baryta in the partial precipitations. As however it was possible that one or other of these portions of acid might be free from certain constituents of the fatty acids, by which their purification might be rendered more easy, M. Heintz investigated each portion separately.

The small quantity of fatty acids which had been last separated in combination with baryta was only sufficient to show, that a small quantity of oleic acid, or of some other acid containing in its hydrated state fewer equivalents of hydrogen than of carbon, is contained in it. This portion of acid was a mixture of small quantities of various acids.

The portion of acids first separated from the æthal, which contains the principal mass of the acids formed by the saponification of the spermaceti, was dissolved in a small quantity of boiling alcohol. The acids which separated on cooling were repeatedly pressed with a powerful press, in order to remove any oleic acid which might be present. The solid acid thus obtained was separated into several portions by precipitation with acetate of baryta. The portion of acid first precipitated in combination with baryta contained an acid, which by recrystallization attained a melting-point of 147° F. This portion probably contained *stearophanic acid*, which however could not be obtained in a pure state, being present in too small quantity.

The next portion gave, by recrystallization, a considerable quantity of pure *margaric acid*, which was recognizable by all its properties and by its composition.

The third portion furnished by repeated recrystallization perfectly pure *palmitic acid*.

From the fourth portion no pure acid could be obtained by mere recrystallization. M. Heintz therefore united it with the portion of acid separated by expression from the cold alcoholic solution, after

* Chem. Gaz., vol. ix. p. 361.

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this had been changed into a lead salt and freed from oleate of lead by extraction with æther. It appeared that the æther did not extract pure oleate of lead, but also a compound of an acid, the hydrate of which contained fewer equivalents of hydrogen than of carbon, which however was still mixed with the lead salts of other fatty acids. The æther also dissolved a neutral butyraceous substance, which was difficult of solution in alcohol even when boiling, and the analysis of which gave the formula $C^{8}\ H^{26}\ O^{4}$. It was evidently not perfectly pure.

From the portion of the spermaceti which was more readily soluble in alcohol, M. Heintz succeeded in separating the two following acids:—

Myristic acid, which melts at 112° F., and consists of $C^{28}\ H^{27}\ O^{3} + HO$, and

Cocinic acid, which melts at 94° F., and consists of $C^{26}\ H^{25}\ O^{3} + HO$.

The best mode of obtaining the latter pure was, by converting the last portion of acid which was precipitated with baryta and which melted at 91° F. into the magnesia salt, by dissolving it in a small portion of alcohol with the addition of ammonia, and precipitating with an alcoholic solution of acetate of magnesia. The cocinate of magnesia remains dissolved in the alcohol. The fatty acid prepared from it can be purified by recrystallization from diluted alcohol.

Lastly, the portion of baryta salt which was separated from the æthal by means of æther, furnished an acid the melting-point of which was at 92° F. By recrystallization however the melting-point rose to 148° F. The acid thus obtained solidified exactly like margaric acid, and no doubt it contained that acid together with small quantities of other acids. The alcoholic solutions, from which this acid was separated, were saturated with ammonia, and precipitated with acetate of lead dissolved in alcohol. The lead precipitate was washed and exhausted with æther, to remove oleic acid. It was found that the acid contained in the dissolved salt of lead contained fewer equivalents of hydrogen than of carbon, and was to be considered as a mixture of oleic acid, or of some fatty acid of analogous composition, with other fatty acids. The acid separated from the lead salt, which was insoluble in æther, contained, together with small quantities of margaric, palmitic, myristic and cocinic acids, a fifth acid, which M. Heintz calls *cetic acid*. It was obtained in this manner:—The margaric and palmitic acids were separated by precipitation with only a small quantity of baryta; the acid remaining dissolved in the alcohol was neutralized with ammonia, and mixed with acetate of magnesia; the liquid was separated from the precipitate, the acid again separated from the latter, and treated once more in the same manner. Lastly, the acid again separated from the magnesia was recrystallized until its melting-point remained constant.

This acid, cetic acid, melts at 135° F., solidifies in concentrically-grouped laminæ with a pearly lustre, and consists of $C^{30}\ H^{29}\ O^{3} + HO$.

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According to this investigation, spermaceti consists of compounds of æthal or oxide of cetyle with margaric, palmitic, cetic, myristic and cocinic acids. M. Heintz gives the following names to these compounds:—

1. Margæthal = margarate of oxide of cetyle.. $C^{34}H^{33}O^3 + C^{32}H^{33}O$.
2. Palmæthal = palmitate of oxide of cetyle.. $C^{32}H^{31}O^3 + C^{32}H^{33}O$.
3. Cetæthal = cetate of oxide of cetyle..... $C^{30}H^{29}O^3 + C^{32}H^{33}O$.
4. Myristæthal = myristate of oxide of cetyle.. $C^{28}H^{27}O^3 + C^{32}H^{33}O$.
5. Cocinæthal = cocate of oxide of cetyle.... $C^{26}H^{25}O^3 + C^{32}H^{33}O$.

A small quantity of oleic acid also appears to be amongst the products of the saponification of spermaceti. At the same time there is also some glycerine in it, no doubt proceeding from the oil from which the spermaceti has crystallized. The oleic acid which is apparently present is therefore probably mixed with the spermaceti as oleine. The two neutral substances which M. Heintz found with the æthal amongst the products of the saponification of spermaceti are also perhaps contained therein in combination with the acids. This is certain of the one which is so readily soluble in alcohol, and which ought therefore to have been extracted from the spermaceti by cold alcohol, but was not. Of the other, it is doubtful. Both substances however are formed in such small quantities from the spermaceti, that they must be considered as inessential constituents of that substance. They are perhaps products of the oxidation of the æthal produced by respiration.

It is remarkable, that, by the saponification of spermaceti, an entire series of fatty acids is formed, without the omission of a single member. It is probable that this series includes six members, from stearophanic acid to cocinic acid. The compound which is richest in carbon is probably always first formed, and then changed, by the gradual action of the oxygen introduced by respiration into the organism of the Cetacea, into the other members of this series with elimination of carbonic acid and water, just as by the action of nitric acid upon oleic acid and proteine substances, a large number of acids of the same series are formed, which however have lost more carbon and hydrogen in consequence of the greater energy of the process of oxidation.

Lastly, M. Heintz has succeeded in proving that the acid resulting from the action of potash-lime upon æthal, at a temperature of 410°–428° F., is a mixture of several acids, of which palmitic acid is no doubt the principal constituent; for by double partial precipitation of the so-called æthalic acid with acetate of baryta, M. Heintz obtained an acid which melts at 142° F., and behaves exactly like palmitic acid. M. Heintz proposes to study the products of the action of potash-lime upon æthal still more carefully.—*Berlin Monatsbericht*, 1852, p. 326.

On Tyrosine. By R. Piria.

The following process may be employed with great advantage in the preparation of tyrosine from horn. A mixture of 3 litres of

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water with 1300 grms. of commercial sulphuric acid is to be made, and heated in a leaden vessel almost to boiling; 500 grms. of horn shavings are then to be added by small quantities at a time, and the whole allowed to boil for about forty-eight hours. The liquid is now to be diluted with much water, and the free acid neutralized with hydrate of lime. It is then to be filtered, the filtrate boiled for one or two hours with some milk of lime, in order to decompose the sulphurous substance and completely decolorize the fluid. The liquid is to be again filtered and evaporated at a temperature near its boiling-point, during which a slight but constant stream of carbonic acid is passed through it. The precipitation of the lime by carbonic acid is the most difficult, but at the same time the most essential part of this process, for the lime is only precipitated very gradually and when exposed to heat; on this account the introduction of the carbonic acid must be continued during the whole course of this operation. It appears even that if a certain temperature be exceeded, the carbonate of lime first precipitated is redissolved; and in order to avoid this evil, it is as well to filter the liquid from time to time, and to subject the filtrate anew to the operation of carbonic acid. In operating with the quantities above given, the evaporation may be interrupted when the fluid is concentrated to 2½ or 3 litres; if it be then allowed to stand quiet till the next day, the tyrosine crystallizes from it. By evaporation of the mother-liquor, leucine mixed with a little tyrosine is obtained. It frequently happens, that, in spite of the employment of the greatest care, nothing crystallizes from the cooled fluid; it must then be again heated, and carbonic acid passed through it as long as any carbonate of lime is separated.

The following is a reaction by which tyrosine may be readily detected, even when it only amounts to 5 or 6 milligrms. By the action of sulphuric acid upon tyrosine, a tyrosino-sulphuric acid is formed, the neutral salts of which strike a deep violet colour with chloride of iron. Some tyrosine (a few milligrammes) are to be put into a watch-glass, and moistened with 1 or 2 drops of sulphuric acid; the glass is then to be covered and allowed to stand for half an hour, when the mixture is to be diluted with water, the acid saturated while hot with carbonate of lime, and filtered; if a few drops of solution of perchloride of iron, containing no free acid, be added to the solution, a rich violet colour is immediately produced, which is very similar to that given by salicylous acid, with perchloride of iron.—*Ann. der Chem. und Pharm.*, lxxxii. p. 251.

Result of some Experiments on the Chemical Action of Light. *By* J. W. Slater, Esq.*

These experiments were undertaken chiefly in order to examine the law proposed by Grothuss, that substances are most readily decolorized by rays of light of a colour complementary to their own. The solutions used for isolating the different rays were, bichromate

* Communicated by the Author.

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of potash for yellow, mixed chlorides of copper and iron for green, ammonio-sulphate of copper for blue, sulphuric tincture of roses for red, and water with a little nitric acid for white. The vessels containing these solutions stood on a shelf about 12 feet from the ground, and had free sunshine through the day. In the first place, five test-tubes containing a strong solution of permanganate of potash were placed respectively in the five rays. The order of decomposition was blue, red, white, green, yellow. The two first were nearly colourless on the third day, and on the seventh, when opened and tested, contained no manganese in solution. The white and green were not entirely decomposed till the twenty-second day, and the yellow after eight weeks still contained much permanganic acid. In order to determine what was the effect of free contact with the atmosphere upon actinic decompositions, two tubes containing solution of permanganate, the one sealed, the other open, were fixed in phials of the ammonio-sulphate of copper, and cemented to the necks so as to prevent the escape of ammoniacal fumes. In about eight hours the solution in the sealed tube had become colourless, whilst the other retained a deep red tinge. Peroxide of mercury exposed to blue light in a sealed tube was much blackened in four days, whilst a similar portion in an open tube was not affected. Periodide of mercury (prepared by trituration) in sealed tubes and dry gave the following order of action,—blue, red, white, green, yellow; the action of the two latter rays being hardly perceptible, and possibly due to small portions of blue and red light which had not been absorbed by the solutions. In unsealed vessels the action was rather less rapid. Covered with water, the iodide was not affected by any of the rays. This salt is far more stable than is generally asserted. The sample used in these experiments had been kept for ten years in diffused light without any alteration, and even in the blue ray an exposure of several weeks was required to produce any great effect. Periodide obtained by precipitation seemed rather less stable.

Iodide of starch, perfectly dry, gave the following order:—Blue, red, white, yellow, green. The decomposition under the two latter rays was very slow and imperfect. When moist, the iodide was bleached far more rapidly than when dry; more rapidly also in open than in closed tubes. Perchloride of mercury was acted on as follows:—Blue, red, white, green. The yellow ray caused no perceptible formation of protochloride. This substance, under the blue ray, gives false results if not perfectly screened from ammoniacal vapours. Peroxide of mercury gave blue, red (considerable), white, green, yellow (very slight). Alcoholic tincture of the green colouring matter of leaves was decomposed very rapidly, and almost simultaneously in all the rays; apparent order, white, red, yellow, green, blue. Alcoholic sulphocyanide of iron gave—white, blue, yellow, green, red. To determine whether the actinic decomposition of solutions was in any way influenced by their degree of concentration, seven sealed phials were placed in white light, each containing 40 parts by measure of concentrated aqueous solution of perchloride of mercury. To No. 2 had been previously added 20 volumes of

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distilled water; No. 3, 40 pts.; No. 4, 80 pts.; No. 5, 120 pts.; No. 6, 160 pts.; No. 7, 330 pts. The decomposition was most rapid in No. 6, then Nos. 5 and 4. The statement that the blue ray deprives salts of their water of crystallization, could not be verified with oxalate of ammonia and ferrocyanide of potassium. Weighed portions of these salts, placed respectively under blue, white and green glasses, were found at the end of a month to have suffered no change in weight. It has been observed by Hunt, that a solution of bichromate of potash gives a greenish-yellow precipitate with sulphate of copper in the sunshine. This was found to take place almost equally in all the rays, whether in sealed or open vessels, though a little earlier in the former. The action was found more rapid and more complete in dilute than in concentrated solutions. The latter, after having ceased to deposit, give a further amount of precipitate if diluted. There is a considerable effervescence in the liquid, caused by the escape of oxygen gas. The precipitate is at first of a greenish-yellow, but becomes a yellowish-brown when dry, and shrinks greatly in bulk. Solutions of sulphate of copper and of bichromate, exposed separately to the sun, and then mixed in the dark, give the same precipitate; but if prepared in the dark, no perceptible precipitate is obtained, even on long standing. If the mixture is boiled, however, a precipitate appears. If the precipitate formed by the action of the sun is removed and the liquid boiled, a precipitate appears of a redder shade, probably identical with Bensch's chromate of copper. I have not as yet obtained a quantity sufficient for analysis, either of this or of the former precipitate. Whether the electric and hygrometric conditions of the atmosphere exert any influence upon actinic decompositions, I have not been able to determine with certainty.

On Meconic Acid, and some of its Derivatives.

By Mr. HENRY HOW, *Assistant to* Dr. Anderson.

[Concluded from page 307.]

Meconamidic Acid.—When æthylomeconic acid is dissolved in warm water or alcohol, and an excess of strong aqueous or alcoholic solution of ammonia is added, the fluid assumes a deep yellow colour, and becomes very soon filled with a yellow semi-gelatinous-looking substance, which, after being washed with dilute spirit, dries up in the air to an amorphous mass, which powders with some difficulty to a very fine yellow powder. This substance, when dissolved in hot water, smells of ammonia, and the solution gives with dilute fixed alkalies abundant evidence of its containing this body as a base. I was at first of the opinion that it was the neutral salt of an amide acid corresponding to æthylomeconic acid, and formed from it in the manner characteristic of the action of ammonia in these cases, in which 1 atom takes the place of an equivalent of alcohol. Upon submitting it to analysis, however, I found this not to be the case; and it appears to me to be the result of a complicated decomposition, which is, so far as I am aware, without analogy. Upon

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adding to its solution in hot water some hydrochloric acid, a white precipitate is obtained, which I presume to be the acid of the compound. I will first give its analysis, and the formula I deduce from it, to render more clear the only constitution I can assign to these two bodies. The following analyses were performed on specimens of different preparations; the acid was recrystallized from boiling water, when it appeared as a white crystalline crust or rind:—

Carbon	39·73	39·65	39·50	84	504	39·84
Hydrogen	3·30	3·32	3·26	39	39	3·08
Oxygen	..	..	..	78	624	49·34
Nitrogen.....	7·84	8·05	7·70	7	98	7·74

The first glance at the above formula reveals a very complex atom, yet in the following scheme its derivation seems at least possible. 7 atoms of ammonia react on 6 of the acid æther:—

6 atoms æthylomeconic acid, $C^{18} H^{8} O^{14} = C^{108} H^{48} O^{84}$ + 7 atoms ammonia, $H^{21} N^{7} = C^{108} H^{69} O^{84} N^{7}$.

$C^{108} H^{69} O^{84} N^{7}$ — 6 atoms alcohol, $C^{24} H^{36} O^{18}$ + 6 atoms water, $H^{6} O^{6} = C^{84} H^{33} O^{78} N^{7}$.

If we consider the above as its derivation, and the 6 atoms of water as water of crystallization retained at 212°, the acid will be $C^{84} H^{33} N^{7} O^{72}$; upon examining this, it is found to contain the elements of 6 atoms of normal amidomeconic acid, corresponding to æthylomeconic acid plus an equivalent of ammonia—

$$C^{84} H^{33} N^{7} O^{72} = 6(2HO, NH^{2} C^{14} HO^{10}) + NH^{3}.$$

A comparison of the numerical per-centages required by the formula of the normal amidomeconic acid with those really obtained, is here given to show how widely they differ—

Carbon	39·62	14 =	84	42·21
Hydrogen	3·29	5	5	2·51
Oxygen	..	12	96	48·25
Nitrogen.....	7·86	1	14	7·03

Yet that the acid in question is really an amidogen compound resulting from meconic acid is to be inferred from the fact, that when it is heated with solution of potash, ammonia is evolved in quantity, and the fluid gives with hydrochloric acid a crystalline precipitate, to be recognised as bimeconate of potash, which, upon subsequent treatment in the same manner, furnishes the characteristic scales of meconic acid. This is the deportment of an acid amide.

The appropriation of the atom of ammonia among the 6 atoms of amidomeconic acid, if indeed this be the constitution of the compound acid produced, seems to have much diminished the basicity of the complex atom, or else the yellow salt is not a neutral one. The amidomeconic acid being bibasic, 6 of its atoms should, in forming a neutral salt, take up 12 equivs. of ammonia, but a considerably less amount is found in the yellow ammonia salt. This is shown in the following analyses; they were performed on specimens prepared at different times and dried at 212°:—

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Carbon	36·47	36·38	..	..	84=504		36·23
Hydrogen	4·60	4·96	..	..	63	63	4·52
Oxygen	..	..	..	..	75	600	43·01
Nitrogen	..	15·99	16·08	15·86	16	224	16·24

The formula expressive of the constitution of this substance as an ammonia salt of the above acid is $9NH^4O, C^{84}H^{24}N^7O^{63}+3Aq$. And the acid itself, considered with regard to its amount of basic water as indicated in the salt, is represented thus:—$9HO, C^{84}H^{24}N^7O^{63}+6Aq$. I attempted to determine directly the amount of nitrogen existing in the yellow salt as ammonia; but, upon reflection, I despaired of success, because the only method at my disposal being to decompose by hydrochloric acid, and evaporate the solution filtered from the precipitated amidic acid with bichloride of platinum, I saw that if this acid behaved as amidogen acids are known to do in concentrated acid fluids, namely to regenerate the parent acid and ammonia, I should inevitably obtain an excess. Nevertheless I made the experiment, and the lowest result I obtained was 10·4 per cent. nitrogen; now 9·08 corresponds to 9 atoms of nitrogen. I also attempted to form other salts by precipitation of solutions by that of the ammonia salt, but the results were unsatisfactory and inconstant. The silver salt, a yellow gelatinous precipitate, dried up to a black mass; and the baryta compound, a yellow amorphous precipitate, insoluble in boiling water, gave varying numbers on analysis.

I have nothing to add descriptive of the acid to what little has been mentioned. It is a white powder as precipitated by acids from the yellow compound, crystallizing from concentrated solution in hot water in a crystalline crust.

The yellow salt has a peculiar appearance. It does not present the least crystalline structure even under the microscope, but consists of round translucent granules; when deposited slowly from dilute fluids, these have the appearance of small yellow vesicles or air-bubbles. It is readily soluble in hot water, with a decided smell of ammonia; it is very sparingly soluble in hot, insoluble in cold alcohol. It gradually loses ammonia when heated in the dry state at 212° F.; at a higher temperature it blackens and fuses.

I have adopted the name of *meconamidic acid* for the acid of this salt, as simply expressive of its constituents, without any reference to the molecular arrangement of its elements.

Coupled Acid Æther of Meconic Acid.—The substance I have described as occurring in the process of making the æthers of meconic acid, when rectified spirit is employed, is deposited generally after the first product of æthylomeconic acid is filtered off. I have sometimes observed it also falling from the mother-liquor, from which the first deposit had been crystallized, and also in the course of purification of the residue left on evaporation of the original acid mother-liquor. Its constant occurrence induced me to examine if it were a substance of determinate composition; I accordingly redissolved some of it in hot water, in which it is extremely soluble, twice or thrice, and obtained, on cooling of the liquid, a white amor-

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phous powder. I select the analyses of two specimens, dried at 212°, treated in this manner:—

Carbon.....	44·80	44·53	32 =	192	44·85
Hydrogen	3·12	2·73	12	12	2·80
Oxygen	..	..	28	224	52·35

I am inclined to think the approximation of the above numbers to the per-centages corresponding to the formula given, in a substance purified from different preparations, is too close to be accidental, and that the body in question is a determinate compound. The formula given contains the elements of 1 atom of meconic and 1 of æthylomeconic acid—

$$C^{32} H^{12} O^{28} = 3HO, C^{14} HO^{11} + 2HO, C^{4} H^{5} O\, C^{14} HO^{11}.$$

A substance of such constitution may be easily imagined to occur, when an insufficient quantity of acid gas had been employed to remove all the water from the meconic acid, or its power had been diminished in this respect by the ready formed water existing in the fluids.

That the substance is something more than an accidental mixture is to be inferred from the action of ammonia. When its warm aqueous solution is supersaturated by strong ammonia, the fluid becomes yellow; but none of the yellow amidic salt is deposited, as might be expected in a mixture containing æthylomeconic acid. If, however, to a concentrated aqueous ammoniacal solution strong alcohol be added, a deposit in small radiated yellow silky tufts appears; and when such an aqueous solution is evaporated to dryness at 212°, a crystalline residue remains, part of which is extremely sparingly soluble in boiling water; the more soluble portion gives with hydrochloric acid a crystalline precipitate in the form of needles. I have not followed out the changes which these few experiments seem to indicate, for my material was small in quantity, and I had no means of readily preparing it tolerably pure at will.

I have called this substance *meconoæthylomeconic acid*, as the name expresses most distinctly the constitution deduced from analysis, and represented by the formula given. I was anxious to have substantiated its constitution as such by a determination of its saturating capacity, but was unable to effect my purpose, owing to the impossibility I experienced of obtaining its salts. When it is treated with bases, the salts produced decompose into meconates with greater facility than those of æthylomeconic acid.

Meconic Æther containing 2 equivs. of Æther.

Biæthylomeconic Acid.—This substance is found in considerable quantity in the acid mother-liquors from which the bodies before described have deposited, especially when absolute alcohol has been employed; its proportionate amount appearing to depend on that of the hydrochloric acid gas employed. It remains, on evaporation of the liquid, till acid ceases to be evolved at 212° F., as a thick oil or viscid mass, becoming a solid crystalline mass on cooling. It may be rendered pure by two or three crystallizations, these serving to

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remove any of the former-mentioned bodies, of which small quantities are generally present in the residue left on evaporation. It is thus obtained in colourless flattened prisms. The analysis of the substance, dried *in vacuo*, is as follows:—

Carbon.....	51·33	51·35	22 =	132	51·56
Hydrogen	4·81	4·84	12	12	4·68
Oxygen	..	..	14	112	43·76

These numbers lead to the formula $HO, 2C^4 H^5 O, C^{14} HO^{11}$.

Having thus far succeeded in replacing 1 and 2 of the atoms of basic water of meconic acid by corresponding equivalents of æther, I was in hopes of being able to go still further, and obtain a neutral compound. For this purpose I distilled some meconic acid with absolute alcohol and strong sulphuric acid. By application of a gentle heat, tranquil ebullition was commenced and sustained. The distillate consisted of alcohol and æther, and the contents of the retort gradually acquired a syrupy consistence; at this period they were poured into a comparatively large quantity of cold water; in a short time a crystalline precipitate of a delicate rose-pink colour was formed, which gradually increased in quantity. On recrystallization from water, it was obtained in colourless flattened prisms, which, dried at 212°, gave on analysis 51·22 of carbon and 4·88 of hydrogen, and show the substance to be identical with that obtained in the former process. This method obviously furnishes a ready source of the pure æther. I may mention that I have not been able to produce it this way by employing rectified spirit in place of absolute alcohol.

Biæthylomeconic acid, in its pure state, as crystallized from water, occurs in the form of long, flattened, colourless prisms; it fuses under boiling water before dissolving. It is very soluble in alcohol. In the dry state it fuses at about 230° F. to a yellowish transparent liquid.

Its aqueous solution readily coagulates the white of eggs, has an acid reaction, and decomposes carbonates with effervescence. It imparts to persalts of iron a red colour.

As the above formula indicates, it is a monobasic acid; I add the analysis of two salts which show this fact.

When subjected to the action of ammonia in the cold, biæthylomeconic acid does not undergo decomposition; the substances simply enter into combination.

Biæthylomeconate of Ammonia.—Some of the æther was dissolved in strong, nearly absolute alcohol, and dry ammoniacal gas was passed into the fluid; the whole soon became a nearly solid yellow mass. When this was freed by pressure from the ammoniacal alcohol, it was found to crystallize from hot spirit in tufts of radiated, silky, yellow needles. Dried *in vacuo*, it gave on analysis—

Carbon	48·04	22 =	132	48·35
Hydrogen.....	5·64	15	15	5·49
Oxygen.....	..	14	112	41·04
Nitrogen	5·46	1	14	5·12

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Its constitution is evidently represented by the formula NH^4O, $2C^4H^5O$, $C^{14}HO^{11}$. It crystallizes without water.

Biæthylomeconate of ammonia is readily soluble in cold water to a yellow fluid; acids precipitate from this the unchanged æther. Its aqueous solution gives the following reactions:—With nitrate of silver, a yellow gelatinous precipitate, insoluble in boiling water, and apparently unaltered by the elevation of temperature; with sulphate of copper, a green gelatinous precipitate; with acetate of lead, a heavy yellowish-white; and with sulphate of magnesia, a crystalline precipitate; with the chlorides of barium, strontium and calcium, it produces pale yellow semi-gelatinous precipitates, insoluble in boiling water, but readily soluble in excess of the earthy salts. A determination of the base in the baryta salt, dried at 212°, gave 23·54 per cent. of baryta; the formula for biæthylomeconate of baryta, $BaO, 2C^4H^5O, C^{14}HO^{11}$, requires 23·68.

I believe, from an experiment made on a small scale, that biæthylomeconic acid, when *heated* with ammonia, undergoes a change; the result is probably an acid amide. Want of material, however, has prevented me as yet from arriving at a satisfactory conclusion on this point.

On Rubian. By Prof. Rochleder.

I some time since published an investigation* of madder, which amongst other things has led to the knowledge of a crystalline yellow substance, to which I assigned the name ruberythric acid. Dr. Schunck's investigation on this subject has since appeared. He has prepared a substance which he calls *rubian*, and has investigated its products of decomposition.

I am convinced the rubian of Dr. Schunck is nothing but impure ruberythric acid. A comparison of the composition and properties of the two bodies may find a place here:—

	Rubian. Average.	Ruberythric acid. Average.
Carbon	54·85	54·48
Hydrogen	5·57	5·16
Oxygen	39·58	40·36

Schunck's rubian gives red precipitates with lime and baryta water; its solution becomes blood-red on the addition of caustic soda; a purple-coloured fluid is produced by boiling, in which the addition of acids throws down yellow flakes. By heating, alizarine is produced. Rubian is precipitated by a solution of basic, but not by neutral acetate of lead. This is exactly the behaviour of ruberythric acid.

Rubian, however, according to Schunck, is amorphous, leaves ashes on combustion, and gives, when warmed with muriatic or sulphuric acid, besides alizarine and sugar, three other products,—*rubianine*, *verantine* and *rubiretine*; whilst ruberythric acid crystallizes, leaves no ash, has no remarkable taste, and only furnishes

* Chem. Gaz. page 23 of the present volume.

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alizarine and sugar when treated with muriatic or sulphuric acid, which gave on analysis 69·56 C, 4·00 H, and 26·44 O, and so could not be contaminated with any remarkable quantity of any foreign body.

If Dr. Schunck will employ the process given by me for the preparation of ruberythric acid, I am convinced that, instead of the amorphous rubian, he will obtain the crystallized ruberythric acid, which I have found in Dutch, Turkey and Hungarian madder, and which is certainly also contained in Avignon madder.—*Ann. der Chem. und Pharm.*, lxxxii. p. 215.

On the Tannic Acids, and a new Class of Nitrogenous Derivatives of the Tannic Acid Series. By A. *and* W. Knop.

Very recently, that series of acids which is distinguished by a high atomic weight, by containing a large number of equivalents of oxygen, and by the property of absorbing a large quantity of oxygen under the influence of alkalies, has become of extraordinary interest. If we characterize these acids generally by the name of tannic acids, this denomination includes, together with quercitannic acid, the acids found in the lichens, and others which form series branching off in various ways in accordance with determinate laws. These acids are distributed through the most various families of plants, and have hitherto presented, in regard to their occurrence, and the manner in which they accompany vegetable bases and vegetable colouring matters, or are connected with these last, many points which have been often alluded to both by chemists and physiologists. Lastly, there are members of this very class which have been shown to contain in their composition a group of elements in such a form, that they are eliminated as sugar, or at least as a so-called hydrate of carbon. Experimental proofs in favour of such a composition have recently been furnished by Higgin, Schunck, Strecker, and Rochleder and his pupils.

For all this, these acids certainly still deserve a careful study, as their salts have not hitherto been sufficiently examined; the atomic weight even of the commonest members of the series is still doubtful. This circumstance arises evidently from the difficulty met with in procuring combinations of these acids of correct chemical composition, because the acids, when united with bases, are either readily altered or form insoluble or uncrystallizable salts.

The salts of these acids with alkaline bases are soluble in water, and would be suited for the preparation of compounds insoluble in water, if they did not possess the property of absorbing oxygen from the air. It appeared therefore probable that the preparation of the salts would succeed if their oxidation were prevented by the presence of some substance which had equally the property of absorbing oxygen.

Starting from this point, we have treated several acids of this class with sulphite of ammonia. The volatility of the sulphurous acid and the energy with which the salt becomes oxidized in the air,

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gave reason to suppose that by this means the fixed tannic acids would produce their ammoniacal salts, and that these would remain protected from oxidation by the action of the excess of sulphite of ammonia. The experiments have, in the first place, confirmed this supposition; and, in the second, have led also to the discovery of a new method, of universal application, for the preparation of nitrogenous derivatives of this series, which can no longer be considered as mere ammoniacal salts, but may rather be regarded for the present as a series of amides.

We propose therefore to submit the various tannic acids to a complete examination in this point of view. We communicate now however only the first results, which we have obtained by treating quercitannic and gallic acids with sulphite of ammonia, remarking nevertheless that similar results have presented themselves in preliminary experiments with some other acids of this series.

If a mixture of about 1 part of perfectly-saturated sulphite of ammonia with 5–6 parts of ammonia be added to an alcoholic solution of quercitannic acid, the fluid becomes very hot, a remarkably large quantity of ammonia becomes combined, and the liquid becomes in consequence of a darker colour, but by no means in the same manner as when the tannic acid is boiled alone with ammonia. By alternate additions of ammonia and sulphite of ammonia, it may be observed, that the colour, which is increased by the addition of the former, is removed again by the latter. The colour attains a certain intensity, and then proceeds no further. As soon as a sufficient quantity of the mixture has been added to make the whole smell slightly of ammonia, the product is evaporated in the water-bath, by which means a sticky brown mass of a peculiar odour is obtained.

This mass is a complicated product, the investigation of which alone will occupy us for a considerable time yet, as it proves different according to the degree in which the alcohol is weakened by the addition of ammonia, and according to the proportions of ammonia and sulphite of ammonia employed. It contains, or at all events gives by the following further treatment, various quantities of the new substance described below, and of a brown uncrystallizable residue, which is chemically combined with sulphurous acid, and not improbably contains the hydrate of carbon which is produced by the decomposition of the tannic acid, and also, apparently under other circumstances, gallate of ammonia. If we proceed according to the data given above, and then boil the mass with alcohol, the liquid separates into two layers. The upper and clearer of these is to be poured away from the lower semi-fluid brown mass; the latter is to be exhausted repeatedly with boiling alcohol, and the united extracts evaporated. On the evaporation of the alcohol, a white mass of small crystals is separated, which is to be collected and purified by recrystallization from a watery solution. In order to free it from any other organic acids which may be mixed with it, it is dissolved in water acidified with muriatic acid, in which it is somewhat more difficult of solution than in pure water. It is obtained in beautiful laminar crystals of a quarter of a square inch in

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size, principally in extremely thin tables of a line square, and of a beautiful fatty lustre, which appear quadrate to the naked eye; also as dazzling white tablets, which are very sensitive to salts of iron. This substance has many properties in common with gallic acid; it is impossible not to see that the characteristic nucleus of the gallic and tannic acids is still contained in it. It contains nitrogen, and is a weak acid, and is consequently a kind of amidogen acid. We will call it for the present *tannigenamic acid* until we have better ascertained the nature of this substance by further investigations, and only describe now its principal characteristics.

Crystallized from its solution in much diluted muriatic acid, and treated upon a filter free from iron, it is obtained in dazzling white, thin laminar crystals, of a strong fatty lustre, which under the microscope appear to be formed of fine prisms laid one upon another. The one base of these prisms is generally without modification, and appears to the naked eye to intersect the two sides at right angles; but under the microscope a divergence from the right angle is readily perceived. The acute angle under which the base intersects one of the sides of the prism, measured under the microscope 88°; but there were also some crystals in which the base with the edge exactly covered the right-angled cross of the microscope. The other base of the prisms appeared much modified, and generally imperfectly developed.

This substance is difficult of solution in water, but apparently still more so in water acidified with muriatic acid; its solubility is much greater in either liquid when boiling than when cold, and it is therefore readily purified by recrystallization. The smallest quantity of iron contained in the filtering-paper tinges the crystals with a shade of blue, the fatty lustre remaining unchanged. Caustic potash rapidly decomposes the acid, communicating a reddish-brown colour in the same manner as with gallic acid; with solution of ammonia it is also decomposed, and by the action of the air the liquid gradually passes through blue and purple to reddish-brown. On being heated with soda-lime, it furnished ammonia, with which, when sufficient soda-lime is not present, some volatile base, aniline or one of its allies, is mixed.

When mixed with a concentrated solution of chloride of platinum, and heated therewith, with the addition of a few drops of muriatic and nitric acids, nearly the whole of the nitrogen is thrown down as ammonio-chloride of platinum, whilst the acid is completely destroyed with a violent effervescence. With acetate of lead the solution of the acid gives a lead salt, which contains acetic acid. When concentrated sulphuric acid is poured over it, it behaves exactly like gallic acid; it became considerably heated, the mass stiffened, and on the addition of water a white powder was precipitated, which looked like gallic acid. We have not yet analysed and completely examined the acid thus separated, by means of which it is evident, if it passes over into gallic acid when heated with sulphuric acid, that the nature of our acid will be immediately established beyond doubt; it appears however to be unchanged tannigenamic acid.

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The acid here described is sufficiently different in its composition from the gallusaminic acid, procured by Robiquet by treating gallic acid, dried at 266°, with dry ammoniacal gas, at least if his analysis be correct $=NH^2, C^{14} H^6 O^9$; should they be ascertained hereafter to be identical, Robiquet's statement must be incorrect. Our acid, obtained from water containing muriatic acid, has an acid reaction in its concentrated solution, and contains neither sulphur nor chlorine; the residue of its combustion with soda and nitrate of potash, when dissolved in nitric acid, gave no precipitate with solutions of silver and chloride of barium.

Analysis.—The substance was burnt in oxygen with a layer of granular oxide of copper in the anterior part of the tube. The nitrogen was determined by burning with soda-lime. The muriate of ammonia obtained from 1 grm. of the substance, when a solution of potash was poured over it, gave off, together with the odour of ammonia, a distinct odour like that of aniline; if less of the substance be employed, and it be mixed with much soda-lime, the muriatic acid in the receiver remains absolutely colourless, and furnishes a perfectly white muriate of ammonia on evaporation. The gas evolved during the combustion does not burn with the flame of carburetted hydrogen, but with that of pure hydrogen. In order to ascertain any admixture of aniline or a similar volatile base, and to avoid the errors which would arise from it, the muriatic acid was evaporated after the combustion in a previously weighed crucible, and,—1st, the muriate of ammonia obtained weighed; 2nd, changed into ammonio-chloride of platinum, and this also weighed; and 3rd, the amount of platinum contained in the latter determined by ignition. The numbers obtained are as follows:—

1. *Determination of the Water.*—0·361 of the finely laminar crystallized substance prepared by the first process, dried at 212°, gave 0·051 water=13·9 per cent.

0·841 of the same substance, dried at 248°, gave 0·117 water =13·9 per cent.

0·5405 of the substance prepared by the second process, when dried at 248°, gave 0·0775 water=14·3 per cent.

0·925 of the same substance gave 0·131 water=14·1 per cent.

2. *Elementary Analysis.*—0·2884 of the substance, dried at 248°, gave 0·527 of carbonic acid=0·1437 carbon=50·60 per cent. of carbon and 0·104 water=0·01155 hydrogen=4·06 per cent. of hydrogen.

3. *Determination of the Nitrogen.*—0·323 of the substance, dried at 248°, gave the following numbers:—

1. When weighed as muriate of ammonia	0·107=0·028 nitrogen=8·61 p. c. nitrogen.
2. When weighed as ammonio-chloride of platinum	0·408=0·031 nitrogen=9·5 p. c. nitrogen.
3. The quantity of platinum contained in No. 2	0·187=0·264 nitrogen=8·17 p. c. nitrogen.

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It is clear from the last determination, that a small quantity of a base with a higher atomic weight must be mixed with the muriate of ammonia (1.), in consequence of the presence of which, the amount of nitrogen, if calculated from (2.), would have proved too high. These results give the formula $C^{42} H^{20} N^3 O^{23} + 9HO$ for the hydrated acid, or $C^{42} H^{20} N^3 O^{23}$ for that dried at 248°, as follows:—

Carbon	50·60	42 =	252	50·60
Hydrogen	4·06	20	20	4·02
Nitrogen	8·17	3	42	8·42
Oxygen.....	37·17	23	184	36·96

We tried if it were possible to determine the nitrogen in this acid by pouring over it concentrated solution of chloride of platinum, and then heating it with a few drops of nitric and muriatic acids. Some loss took place in consequence of an unexpectedly-violent ebullition; nevertheless the amount of nitrogen calculated amounted to 7·4 per cent., and it appears that, with some substances at least, the nitrogen can be determined in this manner.

As regards the above formula, we abstain here from any further considerations on the constitution of the tannic acid and its connexion with gallic acid, because we believe that we have already found a way by which we shall be able before long to bring further facts to bear upon it. By varying the proportions of sulphite of ammonia and ammonia, and also by operating with sulphuret of ammonium, we have already obtained other substances containing sulphurous acid, and have also prepared some interesting products of the metamorphosis of the new acid. By treating gallic acid with sulphite of ammonia, we have also obtained a perfectly white crystallizable ammoniacal salt fitted for analysis, and prefer therefore to treat of this further in our next memoir. We may however exhibit here, by means of the formulæ, the connexion between the new acid and gallic acid, with especial reference to Strecker's last memoir on tannic acid *. Taking 3 atoms of gallic acid, or regarding the acid itself as tribasic, its ammoniacal salt will

$$= 3(C^{14} H^6 O^{10}) + 3NH^4 O = C^{42} H^{30} N^3 O^{33}.$$

$$\text{Now } C^{42} H^{30} N^3 O^{33} = C^{42} H^{20} N^3 O^{23} + 9HO + HO.$$

According to this, the new acid in its crystallized hydrated state differs from gallate of ammonia by wanting 1 equiv. of water; whilst, when dried at 248°, it differs from the same salt by a deficiency of 10 equivs. of water.

Strecker has lately shown that by boiling with diluted sulphuric acid tannic acid furnishes gallic acid and sugar. He expresses what takes place in this case by the formula—

$$C^{40} H^{18} O^{26}, \text{ tannic acid} + 10HO = 2(C^{14} H^8 O^{12}) + C^{12} H^{12} O^{12}.$$

He has founded his formula of tannic acid upon a new analysis.

It is difficult, from our still imperfect investigations, to bring this formula into connexion with that given above; at least gallic acid, which according to our formula must contain 42 atoms of carbon,

* Chem. Gaz. page 156 of the present volume.

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cannot be formed by the decomposition of tannic acid. For that purpose, Strecker's formula must be raised to at least 60 atoms carbon, when, of course, after the deduction of the gallic acid with 42 atoms of carbon, a hydrate of carbon, $C^{18} H^{3} O^{3}$, would remain over—

$$C^{60} H^{27} O^{39} - C^{42} H^{24} O^{36} = C^{18} H^{3} O^{3}.$$

This last might be changed into sugar in the ebullition with sulphuric acid, which is not at all improbable, as from the reactions of the tannic and allied acids, sugar can scarcely pre-exist in them. As soon as we have analysed the residue of the preparation of tannigenamic acid, as well as the substance formed from this acid by the action of concentrated sulphuric acid, and the gallate of ammonia, we propose to return upon this point.

Lastly, with regard to the name provisionally adopted by us for our new acid, tannigenamic acid, the acid, certainly, in reference to the connexion between the hitherto-known amidogen acids and their ammoniacal salts, is not to be characterized as an amidogen acid, because the number of atoms of water eliminated do not correspond with the number of atoms of ammonia. Should it however appear that the acid produced from it by concentrated sulphuric acid is really unaltered, and not an acid differing from it in the number of equivalents of water, this name, which expresses its derivation and production from ammonia, may appear not inappropriate.—*Chem. Pharm. Cent. Blatt*, xxiii. 417.

ANALYTICAL CHEMISTRY.

New Method of precipitating Oxide of Tin and separating it from other Bodies, and of combining it with Silk, Woollen and Cotton Fabrics. By J. Löwenthal.

While endeavouring to find a simple and accurate means of detecting small quantities of perchloride of tin in protochloride, the author found that alkaline sulphates possess the property of decomposing the perchloride and precipitating hydrated oxide from the aqueous solution, while they do not exercise the slightest influence upon the protochloride when atmospheric air is excluded.

In order to prove that it was the alkaline sulphate and not the water dissolving it which effected the decomposition, Löwenthal made the following experiments.

A gramme of anhydrous perchloride of tin was treated in two experiments with 100 and 60 cubic cent. of cold water. The one solution began to lose its clearness after 2 or 3 hours, the latter not till after 36 hours, then very feebly, and it was not milky until after a week. Having thus ascertained the proportion of water which might be employed without fearing decomposition, he mixed,—

a. 0·5 grm. perchloride with a solution of 1 grm. crystallized

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sulphate of soda in 30 cub. cent. water at 64° F. A precipitate was immediately formed.

b. The experiment *a.* was altered by adding 0·125 grm. hydrochloric acid, 1·12 sp. gr., to the perchloride of tin. The liquid was at first turbid, and after one minute the decomposition was complete.

c. On using 0·25 grm. hydrochloric acid, it was not complete until after 3 minutes, with 0·375 grm. 10 min., with 0·5 grm. 43 min., and with 0·75 grm. of acid the liquid remained clear for several hours.

d. 0·5 grm. perchloride with 0·5 grm. hydrochloric acid and 30 cub. cent. water containing 2·5 grms. crystallized sulphate of soda, were mixed at 64° F.; remained at first clear, and the decomposition was not completed until after 7 minutes.

e. The experiment *c.* with 0·5 grm. acid repeated. The liquid at first clear, immediately gave a precipitate when heated to about 108° F.

f. 0·5 grm. protochloride treated with only 15 grms. water containing 1 grm. sulphate of soda. Liquid at first clear, gave a precipitate when heated which did not disappear on cooling.

g. Metastannic acid long digested with hydrochloric acid and the residue dissolved in water. On the addition of sulphate of soda the decomposition ensued immediately. It follows from these data that,—

1. The decomposition takes place in the cold only when a certain quantity of water is present.

2. In the absence of free acid, with an adequate quantity of water and with about 2 equivs. sulphate of soda to 1 equiv. perchloride of tin, the decomposition takes place immediately.

3. Free acid hinders the decomposition more or less in proportion to its quantity. Its influence may be removed by the careful addition of ammonia. Chloride of ammonium does not cause the decomposition of the perchloride.

4. With equal quantities of free acid the decomposition takes place more rapidly, the greater the quantity of sulphate of soda.

5. Heat favours the decomposition in all cases.

Löwenthal likewise found that the sulphates of magnesia, alumina, protoxide of manganese, iron, zinc and copper, peroxide of iron, produced the same decomposition; moreover, nitrates of soda, ammonia, baryta, zinc and copper.

He found that the precipitate was pure hydrated oxide of tin, and never contained any of the acid of the precipitant. He regards the decomposition to be represented by

$$SnCl^2 + 4NaOSO^3 + 4HO = SnO^2\,2HO\,(?) + 2NaCl + 2(NaO, HO, 2SO^3).$$

Although in this equation 4 equivs. sulphate of soda are given, the decomposition takes place with 2 and even with 1 equiv., but a larger quantity of water is then necessary. In this case acid is set free; however, with a sufficiency of water this does not permanently hinder the decomposition (in which the tendency of the hydrated oxide of tin to separate certainly plays an important part), especially at an elevated temperature. The influence of this latter condition was indeed to be expected, since Fremy has shown that the solution of

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hydrated oxide of tin in dilute sulphuric acid is decomposed by boiling.

It now remained to prove that by this means all the tin present as perchloride was precipitated, and that the separation of the tin and chlorine was complete. The decomposition was effected with sulphate of soda (A) and nitrate of ammonia (B). 100 parts of a solution of perchloride of tin gave the following results :—

	A.		B.	
	Tin.	Chlorine.	Tin.	Chlorine.
1.	4·964	5·976	4·935	5·962
2.	4·975	5·956	4·948	5·971

Consequently 100 parts anhydrous perchloride of tin would contain—

	Calculated.	Found.			
		A.		B.	
		1.	2.	1.	2.
Sn eqt. wt.	45·30	45·37	45·51	45·38	45·32
2Cl eqt. wt.	54·70	54·63	54·49	54·62	54·68
	100·00	100·00	100·00	100·00	100·00

These results show that the separation is effected with great accuracy.

This behaviour of oxide of tin admits of several useful applications ; among others—

1. The detection of tin in almost any liquid.

2. It affords an exact and simple means of quantitatively determining tin, as well as an easy and perfect means of separating it from chlorine and other halogens, from alkalies, &c.

It is of especial worth to manufacturers in determining the commercial value of tin salts. In the absence of delicate balances they generally have recourse to the nitric acid test, which always gives an incorrect result, in consequence of the volatilization of the chloride of tin.

In some experiments on the quantitative separation of oxide from binoxide of tin, I obtained on mixing 9·0723 of the above solution to which a few drops of hydrochloric acid had been added with 10·6196 of a solution of protochloride corresponding to 16 per cent. of protoxide, 0·6792 protoxide of tin corresponding to 0·5339 grm., or calculated for 100 parts of the solution 5·002, consequently only 0·042 per cent. more than the average of the above results, which amounts to 4·960.

3. It affords a very suitable means of combining oxide of tin with cotton, woollen and silk stuffs in dyeing. Löwenstein considers that the experiments made by him justify the opinion that this method, *properly employed**, has great advantages over the use of the expensive alkaline stannates.

4. Dark colours containing tin may be conveniently made by this means.—*Journ. für Prakt. Chem.* lvi. p. 366.

* The mode of employment is not stated by the author.

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THE CHEMICAL GAZETTE.

No. CCXXXVIII.—September 15, 1852.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Description of a New Mineral and a New Earth.

By DAVID D. OWEN, M.D.

WHILE examining, in the summer of 1848, the north shore of Lake Superior, situated in Minnesota, between Pigeon Point and Fond du Lac, particularly in the vicinity of Baptism River, I observed a peculiar soft green mineral diffused in the amygdaloidal traps. Though not in large masses, this mineral was so abundantly disseminated in some of these rocks, that the least blow of the hammer indented the rock, and left a whitish-green mark from the easily-crushed particles of the soft green mineral in question.

In the winter of the same year I undertook a chemical analysis of the mineral, and repeated it on several varieties in the year following.

The result showed it to be essentially a hydrated silicate of magnesia, and what appeared to be a new earth, intermediate in its properties between magnesia and manganese.

The colour of this mineral when pure is of a pale yellowish-green; consistence and hardness about that of wax. Heated in a matrass, it gives off water. Heated strongly alone in the forceps, it whitens, but does not exfoliate; tinges the outer flame slightly green. In thin splinters, it fuses on the edges. With borax it dissolves with difficulty into a transparent bead, which has a greenish tinge when hot. With soda it dissolves but very partially and very slowly. Heated with nitrate of cobalt, hardly any colour is perceptible. Fused with four times its weight of carbonate of soda and potash in a platina vessel, it gives a white enamel, tinged on the edges only of a light blue. Some specimens of this mineral effervesce distinctly with acids, but this is always from impurities. The pure varieties contain no carbonic acid. Specific gravity, 2·548. It has not been found crystallized.

Treated with hydrochloric acid, chlorine is evolved, and the greater part of the constituents, except silica, dissolved.

After the separation of the silica and the greater part of the magnesia, there invariably remained a whitish mass, tinged slightly of a reddish-yellow or flesh colour, which had a tendency to darken in the air; this amounted to 18 or 19 per cent. When this was dissolved in just sufficient hydrochloric acid to take it up, and afterwards boiled with excess of caustic potash, 4·6 per cent. of alumina

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separated, leaving about 13·5 of matter quite insoluble in that reagent; of this 1·5 per cent. was peroxide of iron, and about 12 per cent. the new earth above alluded to, slightly contaminated with magnesia.

The analysis of the mineral is therefore as follows:—

SiO^3	Al^2O^3	Fe^2O^3	New earth	MgO	KO	Mn	HO
42	4·6	1·5	10-12	20·5	0·8	trace	18

It was found exceedingly difficult to free this earth entirely from oxide of iron and magnesia. I succeeded however in separating the iron by the following process, so that the solution no longer gave the reaction indicative of iron either with hydrosulphuret of ammonia or ferroprussiate of potash. The solution was evaporated nearly to dryness, and while still hot a jet of water was thrown on it. By repeating this process several times, the oxide of iron was all precipitated, and could be separated by filtration, though the solution passed with extreme slowness through the filter from the free state of the precipitated oxide of iron. The magnesia was separated by two methods, either by dissolving the earth in hydrochloric acid, adding sal-ammoniac and neutralizing with ammonia, or by digesting the earth in water acidulated with a few drops of nitric acid. In consequence however of the new earth being slightly soluble in sal-ammoniac and in dilute nitric acid, some loss is sustained by this method, and therefore it is not applicable to quantitative analysis.

When thus separated, this earth has the following properties and reaction with reagents:—

It dissolves readily either in hydrochloric or nitric acid, evolving chlorine from the former acid. The solution in hydrochloric acid, when concentrated, has a beautiful pea-green colour, and the salt crystallizes either of a slightly paler green or a light chrome-yellow, depending on the degree of heat at which the evaporation is completed. The peculiar colour of its salts, together with the appearance of the residue left in the analytical process after treating with caustic potash to separate the alumina, was what first attracted my attention to this earth.

The solution of the earth in dilute hydrochloric acid gives the following reactions with reagents:—

Ammonia, a white bulky precipitate, only sparingly soluble in sal-ammoniac. This is one of the characters which distinguish it from magnesia. Oxalate of ammonia, a white precipitate in neutral solutions,—another distinction between it and magnesia. Oxalic acid, no precipitate until quite neutralized by ammonia. Bicarbonate of potash, white precipitate,—apparently slightly soluble in excess. Phosphate of soda and ammonia: the vesicular precipitate with this reagent is quite peculiar, and forms one of the marked characteristics of this earth. If the reagent be added without disturbing the fluid, a number of little vesicles are formed, which remain distinct, as if each were enclosed in a delicate translucent membrane. Ferrocyanide of potassium, a white precipitate, with a slight tinge of bluish-green, which seemed to be independent of any remaining trace of

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oxide of iron, perhaps in part due to the colour of the reagent itself. Hydrosulphuret of ammonia, a white precipitate. Succinate of ammonia, a white precipitate even in slightly acid solutions. Benzoate of ammonia, the same, with a tinge of yellow. Crystals of sulphate of potash, inserted in the solution, gave but a very slight precipitate, and that only after long standing. The precipitate with phosphate of soda is soluble only in a considerable portion of muriatic acid, and is not precipitated by boiling.

When separated, and still slightly contaminated with magnesia, the earth has a pale flesh colour, not unlike yttria. When freed from the magnesia, it has more the appearance of powdered dried albumen.

The earth differs from alumina and glucina in being insoluble in caustic potash. From magnesia, in producing coloured salts; in being only slightly soluble in ammoniacal salts; in the peculiar vesicular character of the precipitate with phosphate of soda; in being precipitated by oxalate of ammonia. From yttria it differs in not giving a precipitate with oxalic acid in slightly acid solutions; in being precipitated by succinate of ammonia, even before the solution is quite neutral, which prevents this reagent being applied to separate iron from it, as is recommended by Berzelius for separating oxide of iron from yttria. It differs from zirconium in being soluble in nitric and muriatic acids after ignition. From cerium, in not turning of a brick-red after ignition; and in the colour of its salts, which are not amethystine, but shades of green and yellow, except the nitrate, which is almost colourless. The nitrate crystallizes in prisms, which seem to be right-rhombic. Its salts, like the corresponding ones of magnesia, seem to be deliquescent.

The mineral from which this earth was extracted differs from talc in the absence of any foliated structure; in not exfoliating before the blowpipe; in giving off water in the matrass, which talc does not, being quite anhydrous, while this is a hydrated silicate. It contains 20 per cent. less silica than talc.

Leaving out of account the earth in question, the chemical constitution of this mineral comes nearest to saponite and soap-stone. The specimens of saponite or soap-stone analysed by Klaproth contain 3 to 4 per cent. more silica, 4 to 5 per cent. more magnesia, 4 to 5 more alumina, and about the same quantity of water and oxide of iron.

The specimens of saponite from Brusksveden, analysed by Svanberg, contain 8 to 9 per cent. more silica, 22 per cent. more alumina, and 10 per cent. less magnesia and 8 per cent. less water.

From the green earth often disseminated in the Italian amygdaloids it differs essentially. Most of these contain a large per-centage of oxide of iron and very little magnesia,—2 to 6 per cent. only. Several of the analyses of serpentine and marmolite indicate nearly the same amount of silica as in this mineral, but in them the magnesia is doubled.

Some specimens yielded a fraction of 1 per cent. of copper, but this is an accidental impurity, like the adhering carbonate; the acid

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solution of the pure mineral gives with sulphuretted hydrogen a slight milkiness only, from a small quantity of precipitated sulphur, caused by the reduction of the small quantity of peroxide of iron present. The green colour of the mineral may probably be attributed to the presence of this peculiar earth, which produces green salts.

In consequence of the difficulty of separating the traces of magnesia, without dissolving part of the earth itself, I have not been able to ascertain the exact per-centage of the earth in the mineral, nor yet determine its combining proportion.

From the quantity of chlorine evolved during the solution of the mineral and the earth in hydrochloric acid, it appears that this earth must exist in at least two degrees of oxidation; the chlorine being disengaged, just as in the case of the solution of the higher oxides of manganese* when treated with hydrochloric acid.

If the small per-centage of alumina and oxide of iron present be regarded as accidental, it is probable that the constitution of the mineral is 2 equivs. of bisilicate of magnesia and 1 equiv. of a silicate of the peroxide of the earth with 2 equivs. of water, or—

$$2MgO, 2SiO^3 + NE, SiO^3 + 2HO.$$

Although most of the water is expelled by a heat below redness, still I think it must be regarded as almost all combined; since the quantity obtained is very uniform, and is within a fraction of a per cent. of 2 equivs.

From the above I conclude, that the earth contained in the mineral, which is nearly insoluble in sal-ammoniac, insoluble in caustic potash, and producing the above reaction with reagents, and green and yellow salts, must either be a new earth, or else a modification of some known earth not previously noticed.

The name *Thalium* is proposed for the base of this earth, *Thalia* for the earth itself, and *Thalite* for the mineral from which it is extracted.—*Journ. Acad. Nat. Sci. Phil.*, vol. ii. part 2, 1852; and Silliman's *Journal*, May 1852.

On a peculiar brittle form of Silver. *By* A. *and* W. Knop.

About a year ago we received from a considerable manufactory of cast-silver articles in Leipzig, some specimens of silver, which were remarkable from their brittleness. This brittle silver was formed in the crucible in which the silver was melted for casting, in the form of a film on the surface, which, when the fluid silver beneath it was poured out, remained attached to the crucible, in the same manner as the oxidated film which forms upon lead or bismuth.

However little interest this phænomenon may possess scientifically, in a technical point of view it is of much consequence, as this residue of brittle and difficultly-fusible silver formed in time no inconsiderable quantity.

* The mere trace of manganese present in the mineral will not account for the quantity of chlorine evolved.

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The silver, as we are informed, was obtained from the Mansfeld works, and was separated from the ore by the new method by means of muriate of soda. The brittle silver was partly in thin leaves of the thickness of the back of a knife, with a porous froth-like surface, and partly in thicker masses. It had a crystalline fibrous structure in the thin porous pieces, which have exactly the appearance of solidified dross, the fibres, as is usual in such circumstances, being perpendicular to the surface of cooling. The specific gravity was 10·25, but the masses were always porous internally. There was also in the inner portions, as was ascertained by analysis, after the most careful cleansing of the surface, some clay and sand, traces of the enclosed dross. Analysis gave—

Silver	97·5
Copper	2·3
$SiO^3 Al^2 O^3$	0·1

This composition gives no reason for the above-described brittleness. The silver, when precipitated anew as chloride of silver, and reduced by means of potash and sugar, possessed its usual ductility. Such silver, when changed into chloride of silver, required precisely the quantity of chlorine corresponding to the atomic weight of the silver. The circumstance consequently could not arise from some unknown kind of admixture or modification of the silver.

That heat produces this phænomenon is not admissible; it appears rather to be caused by the admixture of small quantities of foreign substances, which change the properties of the metal differently at different degrees of heat. On the solution of the silver examined by us, some dense clouds remained, too little to enable us to examine them, but distinctly containing silver. Is it possible that a small quantity of chloride of silver may remain under certain circumstances in the silver, and produce these phænomena? The supposition may also be entertained with regard to iodide, bromide and fluoride of silver.—*Chem. Pharm. Cent. Blatt*, 1852, p. 530.

On the Proximate Principles of Human Urine.
By Dr. W. Marcet.

Notwithstanding the care which has been bestowed upon the study of the proximate principles of human urine, the methods hitherto employed have not enabled the investigators to ascertain exactly the form under which these principles exist in the secretion in question. In the hope of obtaining more precise results, I have made use of a method of isolating the urea of the urine, which has enabled me to obtain it directly, without, as is usually the case, passing through a series of combinations and decompositions. This method of analysis has led me to prove—

1. That almost the whole of the urea exists in a free state in the urine.

2. That healthy urine contains two animal substances with an

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acid reaction, the presence of which in that secretion has hitherto been overlooked.

To arrive at these results I operated in the following manner:—After evaporating to dryness in the water-bath one or two emissions of fresh human urine which possessed an acid reaction, I dried the residue over sulphuric acid; it was then easy to separate the urea by means of boiling absolute alcohol. In order to obtain a very concentrated alcoholic solution, the residue was treated repeatedly with small quantities of alcohol, decanting the fluid after each operation, until the last extract was completely colourless. I perceived then that this solution had a very marked acid reaction; it also contained the whole of the urea existing in a free state in the urine submitted to examination.

Instead of concentrating the extract procured as above, and separating the urea from it by means of nitric or oxalic acid, I added a little sulphuric æther to the solution, pouring it gently down the side of the vessel so as to avoid a rapid mixture of the liquid; by this means two layers were formed, the contact of which produced a cloudy precipitate as the mixture became gradually effected. At the end of a few hours this precipitate had disappeared, and in its place there was a magnificent crystallization of urea, occupying the sides and the bottom of the vessel. By adding æther until it no longer produced any precipitate, I succeeded in crystallizing nearly the whole of the urea contained in the alcoholic solution. In this form it was very deliquescent from the presence of a little common salt, from which I freed it by recrystallization from water after having decanted the acid mixture of æther and alcohol. By this means I obtained the urea in a perfectly pure state, and in sufficient quantity to lead one to conclude that this principle exists in great part, or almost entirely, in a free state, as a proximate principle of human urine.

It appeared to me that this mode of analysis might also serve to ascertain the cause of the acid reaction presented by the urine, by eliminating from the mother-liquor from which the urea had been deposited a small quantity of the substance which it still retained in solution. With this view, after the decantation of the ætherial solution, I concentrated it on the sand-bath, after neutralizing it with a little baryta-water to avoid the decomposition of the acid substances; when the æther and alcohol had completely disappeared, the baryta salt was decomposed by sulphuric acid. On shaking the mixture in a vessel with some common alcohol, I obtained, after filtration, an alcoholic solution of urea with a very acid reaction. This liquid was then washed with water and æther; and on the mixture being allowed to stand, it separated gradually into two layers. The upper layer contained the æther, holding in solution the acid, which communicated to it a fine rose colour; whilst the lower layer consisted of the water and alcohol, containing the urea and sulphuric acid.

To purify the acids contained in the æther, this was washed repeatedly with a mixture of water and alcohol, and then with water alone, decanting the ætherial solution after each operation. In

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order to crystallize the acids, I concentrated the ætherial solution at the temperature of the air; and after twenty-four hours there remained a watery liquid, upon which a multitude of small colourless crystals had formed. A resinous substance, of an intense rose colour, and strongly acid, was deposited on the sides of the vessel.

I readily separated the colourless crystals by filtering the aqueous liquid, when I ascertained that they possessed the following properties:—They crystallize in oblique rhombohedra, are insoluble in cold water, but are dissolved by boiling water. Alcohol and æther dissolved them. In all these cases they communicate an acid reaction to the solution.

The above properties would appear to bring this substance near to hippuric acid; it differs from that substance, however, for on heating the crystals upon a sheet of platinum, they melt, and diffuse a characteristic odour very different from that of hippuric acid. They afterwards become charred without taking fire, and at length disappear entirely.

The rose-coloured substance which was deposited on the sides of the vessel has a more strongly acid reaction than the preceding, but it is insoluble both in cold and hot water; alcohol and æther dissolve it, but only when hot. When heated on a piece of platinum, it diffuses an odour of burnt oil; it then becomes charred, and disappears without leaving any traces. It appears that this substance must exist in the urine in a free state, for I succeeded in obtaining it without the addition of sulphuric acid to the concentrated ætherial solution.

It seems, on the other hand, that the crystallized acid previously described must exist in combination with some other substance, as I have not been able to separate it without the employment of baryta and sulphuric acid, unless indeed it was decomposed by the action of the heat during concentration.

I will add, in conclusion, that these acids did not contain the least trace of sulphuric acid, as I easily ascertained by treating their solution with baryta-water.

Lastly, I have just observed, that after four or five days the rose-coloured substance deposits crystals quite different from those of the other acid. I hope to be able to present some new observations on this subject very shortly.—*Bibl. Univ. de Genève*, 1852, p. 144.

On the Reduction of Metals by Phosphorus and Sulphur.

By W. Wicke.

With reference to the observations published by M. Wöhler*, that phosphorus in combination with copper excites an electrical current, I have made the following investigation:—

1. A stick of phosphorus wound round with a strip of silver was placed in a tolerably-concentrated solution of nitrate of silver. The silver and phosphorus became instantly covered with a blackish film; afterwards silver began to be reduced in a wart-like form upon the

* Liebig's Annalen, vol. lxxix. p. 126.

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strip of silver, and after the lapse of a few weeks it was covered with an extremely shining coating of crystalline silver, although not in immediate contact with the phosphorus. The form of the crystals could not be determined, as they had grown so close together that the whole of the reduced silver could be removed from the strip of silver as a compact coating with a shining inner surface. The phosphorus was only covered superficially with a thin coating of dark phosphuret of silver, and remained unchanged internally. The silver separated so evenly, and with such a shining surface, that this process might perhaps be employed for galvano-plastic purposes.

2. In a similar manner, by a combination of phosphorus and lead in a solution of nitrate of lead, the reduction of crystallized lead took place upon the lead, whilst the phosphorus was covered with a thin black film. The action however was weak, and soon stopped altogether.

3. A stick of phosphorus was placed as the axis of a closely-pressed mass of oxide of copper, both covered with water, with which the tube was filled, and then made air-tight; the reduction of the oxide to metallic copper was gradually effected, so that after the lapse of several weeks the stick of phosphorus, which was still remaining, was surrounded by a capsule of crystalline copper, in which the individual crystals were distinguishable with the naked eye.

4. Sulphur, surrounded by a strip of lead and laid in a solution of nitrate of lead, effected the reduction of lead upon the lead in the form of a loose crystalline coating.

5. When a piece of sulphur, surrounded with a bright copper wire, was laid in a saturated solution of sulphate of copper, it became covered after some time, in the place where the copper touched it, with a loose crystalline coating of indigo-coloured sulphuret of copper, whilst the copper wire was dissolved. A solution of nitrate of copper operated still more rapidly. On the other hand, no action took place on the employment merely of diluted sulphuric acid.—*Ann. der Chem. und Pharm.*, lxxxii. p. 145.

ANALYTICAL CHEMISTRY.

Observations upon a general Method for detecting the Organic Alkaloids in Cases of Poisoning. By Professor Stass *of Brussels.*

Whatever certain authors may have said on the subject, it is possible to discover in a suspected liquid all the alkaloids, in whatever state they may be. I am quite convinced that every chemist who has kept up his knowledge as to analysis, will not only succeed in detecting their presence, but even in determining the nature of that which he has discovered, provided that the alkaloid in question is one of that class of bodies, the properties of which have been suitably studied. Thus he will be able to discover coniine, nicotine, aniline, picoline, petinine, morphine, codeine, narcotine, strychnine,

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brucine, veratrine, colchicine, delphine, emetine, solanine, aconitine, atropine and hyoscyamine. I do not pretend to say that the chemical study of all these alkaloids has been sufficiently well made to enable the experimenter who detects one of them to know it immediately, and affirm that it is such an alkaloid, and not such another. Nevertheless, in those even which he cannot positively determine or specify, he may be able to say that it belongs to such a family of vegetables, the Solanaceæ for example. In a case of poisoning by such agents, even this will be of much importance. The method which I now propose for detecting the alkaloids in suspected matters is nearly the same as that employed for extracting those bodies from the vegetables which contain them. The only difference consists in the manner of setting them free, and of presenting them to the action of solvents. We know that the alkaloids form acid salts, which are equally soluble in water and alcohol; we know also that a solution of these acid salts can be decomposed, so that the base set at liberty remains either momentarily or permanently in solution in the liquid. *I have observed that all the solid and fixed alkaloids above enumerated, when maintained in a free state and in solution in a liquid, can be taken up by æther when this solvent is in sufficient quantity.* Thus, to extract an alkaloid from a suspected substance, the only problem to resolve consists in separating, by the aid of simple means, the foreign matters, and then finding a base which, in rendering the alkaloid free, retains it in solution, in order that the æther may extract it from the liquid. Successive treatment by water and alcohol of different degrees of concentration suffices for separating the foreign matters, and obtaining in a small bulk a solution in which the alkaloid can be found. The bicarbonates of potash or soda, or these alkalies in a caustic state, are convenient bases for setting the alkaloids at liberty, at the same time keeping them wholly in solution, especially if the alkaloids have been combined with an excess of tartaric or of oxalic acid.

To separate foreign substances, animal or otherwise, from the suspected matters, recourse is commonly had to the tribasic acetate of lead, and precipitating the lead afterwards by a current of sulphuretted hydrogen. As I have several times witnessed, this procedure has many and very serious inconveniences. In the first place, the tribasic acetate of lead, even when used in large excess, comes far short of precipitating all the foreign matters; secondly, the sulphuretted hydrogen, which is used to precipitate the lead, remains in combination with certain organic matters, which undergo great changes by the action of the air, and of even a moderate heat; so that animal liquids, which have been precipitated by the tribasic acetate of lead, and from which the lead has been separated afterwards by hydrosulphuric acid, colour rapidly on exposure to the air, and exhale at the same time a putrid odour, which adheres firmly to the matters which we extract afterwards from these liquids. The use of a salt of lead presents another inconvenience, viz. the introduction of foreign metals into the suspected matters, so that that portion of the suspected substance is rendered unfit for testing

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for mineral substances. The successive and combined use of water and alcohol at different states of concentration permits us to search for mineral substances, whatever be their nature; so that in this way nothing is compromised, which is of immense advantage when the analyst does not know what poison he is to look for.

It is hardly necessary to say, that in medico-legal researches for the alkaloids, we ought never to use animal charcoal for decolorizing the liquids, because we may lose all the alkaloid in the suspected matters. It is generally known that animal charcoal absorbs these substances at the same time that it fixes the colouring and odoriferous matters.

The above observations do not proceed from speculative ideas only, but are the result of a pretty long series of experiments which I have several times employed for discovering these organic alkaloids. To put in practice the principles which I have thus explained, the following is the method in which I propose to set about such an analysis:—I suppose that we wish to look for an alkaloid in the contents of the stomach or intestines; we commence by adding to these matters twice their weight of pure and very strong alcohol*; we add afterwards, according to the quantity and nature of the suspected matter, from 10 to 30 grs. of tartaric or oxalic acid,—in preference, tartaric; we introduce the mixture into a flask, and heat it to 160° or 170° F. After it has completely cooled, it is to be filtered, the insoluble residue washed with strong alcohol, and the filtered liquid evaporated *in vacuo*. If the operator has not an air-pump, the liquid is to be exposed to a strong current of air at a temperature of not more than 90° F. If, after the volatilization of the alcohol, the residue contains fatty or other insoluble matters, the liquid is to be filtered a second time, and then the filtrate and washings of the filter evaporated in the air-pump till nearly dry. If we have no air-pump, it is to be placed under a bell-jar over a vessel containing concentrated sulphuric acid. We are then to treat the residue with cold anhydrous alcohol, taking care to exhaust the substance thoroughly; we evaporate the alcohol in the open air at the ordinary temperature, or still better, *in vacuo*; we now dissolve the acid residue in the smallest possible quantity of water, and introduce the solution into a small test-tube, and add little by little pure powdered bicarbonate of soda or potash till a fresh quantity produces no further effervescence of carbonic acid. We then agitate the whole with four or five times its bulk of pure æther, and leave it to settle. When the æther swimming on the top is perfectly clear, decant some of it into a capsule, and leave it in *a very dry place* to spontaneous evaporation.

Now, two orders of things may present themselves,—either the

* When we wish to look for an alkaloid in the tissue of an organ, as the liver, heart or lungs, we must first divide the organ into very small fragments, moisten the mass with pure strong alcohol, then express strongly, and by further treatment with alcohol exhaust the tissue of everything soluble. The liquid so obtained is to be treated in the same way as a mixture of suspected matter and alcohol.

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alkaloid contained in the suspected matter is liquid and volatile, or solid and fixed. I shall now consider these two hypotheses.

Examination for a Liquid and Volatile Alkaloid.—We suppose there exists a liquid and volatile alkaloid. In such a case, by the evaporation of the æther, there remain in the inside of the capsule some small liquid striæ, which fall to the bottom of the vessel. In this case, under the influence of the heat of the hand, the contents of the capsule exhale an odour more or less disagreeable, which becomes, according to the nature of the alkaloid, more or less pungent, suffocating, irritant; it presents, in short, a smell like that of a volatile alkali masked by an animal odour. If we discover any traces of the presence of a volatile alkaloid, we add then to the contents of the vessel, from which we have decanted a small quantity of æther, 1 or 2 fluid drms. of a strong solution of caustic potash or soda, and agitate the mixture. After a sufficient time, we draw off the æther into a test-tube, exhaust the mixture by two or three treatments with æther, and unite all the ætherial fluids. We pour afterwards into this æther, holding the alkaloid in solution, 1 or 2 drms. of water, acidulated with a fifth part of its weight of pure sulphuric acid, agitate it for some time, leave it to settle, pour off the æther swimming on the top, and wash the acid liquid at the bottom with a new quantity of æther. As the sulphates of ammonia, of nicotine, aniline, quinoleine, picoline, and petinine are entirely insoluble in æther, the water acidulated with sulphuric acid contains the alkaloid in a small bulk, and in the state of a pure sulphate; but as the sulphate of coniine is soluble in æther, the æther may contain a small quantity of this alkaloid, but the greater part remains in the acidulated watery solution. The æther, on the other hand, retains all the animal matters which it has taken from the alkaline solutions. If it, on spontaneous evaporation, leaves a small quantity of a feebly-coloured yellowish residue, of a repulsive animal odour, mixed with a certain quantity of sulphate of coniine, this alkaloid exists in the suspected matter under analysis. To extract the alkaloid from the solution of the acid sulphate, we add to the latter an aqueous and concentrated solution of potash or caustic soda; we agitate and exhaust the mixture with pure æther; the æther dissolves ammonia, and the alkaloid is now free. We expose the ætherial solution at the lowest possible temperature to spontaneous evaporation; almost all the ammonia volatilizes with the æther, whilst the alkaloid remains as residue. To eliminate the last traces of ammonia, we place for a few minutes the vessel containing the alkaloid in a vacuum over sulphuric acid and obtain the organic alkaloid with the chemical and physical characters which belong to it, and which it is now the chemist's duty to determine positively.

On the 3rd of March 1851, I applied the process which I have described to the detection of nicotine in the blood from the heart of a dog poisoned by 2 cub. centims. [0·78 C.I.] of nicotine introduced into the œsophagus; and I was able, in a most positive manner, to determine the presence of nicotine in the blood. I was able to determine its physical characters, its odour, taste and alkalinity. I succeeded in obtaining the chloro-platinate of the base perfectly

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crystallized in quadrilateral rhomboidal prisms of a rather dark yellow colour, and to ascertain their insolubility in alcohol and æther.

I have applied the same process to the detection of coniine in a very old tincture of hemlock, which my friend and colleague M. de Hemptinne was so kind as to place at my disposal; and I was equally successful in extracting from the liquid colourless coniine, presenting all the physical and chemical properties of this alkaloid. I was also able to prove that the æther which holds coniine in solution carries off a notable portion of this alkaloid when the solvent is exposed to spontaneous evaporation.

Examination for a Solid and Fixed Alkaloid.—Let us now suppose that the alkaloid is solid and fixed; in that case, according to the nature of the alkaloid, it may happen that the evaporation of the æther resulting from the treatment of the acid matter, to which we have added bicarbonate of soda, may leave or not a residue containing an alkaloid. If it does, we add a solution of caustic potash or soda to the liquid, and agitate it briskly with æther. This dissolves the vegetable alkaloid, now free and remaining in the solution of potash or soda. In either case, we exhaust the matter with æther. Whatever be the agent which has set the alkaloid free, whether it be the bicarbonate of soda or potash, or caustic soda or potash, it remains, by the evaporation of the æther, on the side of the capsule as a solid body, but more commonly as a colourless milky liquid, holding solid matters in suspension. The odour of the substance is animal, disagreeable, but not pungent. It turns litmus-paper permanently blue.

When we thus discover a solid alkaloid, the first thing to do is to try and obtain it in a crystalline state, so as to be able to determine its form. Put some drops of alcohol in the capsule which contains the alkaloid, and leave the solution to spontaneous evaporation. It is however very rare that the alkaloid obtained by the above process is pure enough to crystallize. Almost always it is contaminated with foreign matters. To isolate these substances, some drops of water, feebly acidulated with sulphuric acid, are poured into the capsule, and then moved over its surface, so as to bring it in contact with the matter in the capsule. Generally we observe that the acid water does not moisten the sides of the vessel. The matter which is contained in it separates into two parts, one formed of greasy matter, which remains adherent to the sides; the other alkaline, which dissolves and forms an acid sulphate. We cautiously decant the acid liquid, which ought to be limpid and colourless if the process has been well executed; the capsule is well washed with some drops of acidulated water, added to the first liquid, and the whole is evaporated to three-fourths *in vacuo*, or under a bell-jar over sulphuric acid. We put into the residue a very concentrated solution of pure carbonate of potash, and treat the whole liquid with absolute alcohol. This dissolves the alkaloid, while it leaves untouched the sulphate of potash and excess of carbonate of potash. The evaporation of the alcoholic solution gives us the alkaloid in crystals.

It is now the chemist's business to determine its properties, to be able to prove its individuality. I have applied the principles which I have just expounded to the detection of morphine, iodine, strych-

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nine, brucine, veratrine, emetine, colchicine, aconitine, atropine, hyoscyamine; and I have succeeded in isolating, without the least difficulty, these different alkaloids, previously mixed with foreign matters.

I have thus been able to extract, by this process, morphine from opium, strychnine and brucine from nux vomica, veratrine from extract of veratrum, emetine from extract of ipecacuanha, colchicine from tincture of colchicum, aconitine from an aqueous extract of aconite, hyoscyamine from a very old extract of henbane, and atropine from an equally old tincture of belladonna. Thus it is in all confidence that I submit this process to the consideration of chemists who undertake medico-legal researches.—*Bulletin de l'Académie Royal de Médecine de Belgique*, vol. vi. No. 2; and *Edinburgh Monthly Journal of Medical Science*, Sept. 1852.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On Gutta Percha, its Properties, Analysis, Elementary Composition and Applications. By M. PAYEN.

WITHOUT possessing any exact information regarding the extraction of the substance which comes to us from the Eastern Archipelago under the name of *gutta percha*, we know that this substance is contained in the descending sap of the *Isonandra Gutta*, Hooker, belonging to the natural order Sapotaceæ. This tree attains a great size, being sometimes as much as a yard in diameter and 60 or 70 feet in height; its soft and fibrous wood is useless for industrial purposes; its fruit furnishes a fatty oil.

It is said that a tree, when cut down, will yield 18 kilogrms. of gutta percha or solid gum. The juices, dried in thin strata laid one upon another, form irregular masses of greater or less thickness, of a reddish or grayish colour, of which a gradually increasing quantity has been annually imported into Europe and America since 1845.

During many years, the natives of the countries where it is produced have employed it almost solely in the formation of handles for axes, which possess when cold a certain degree of flexibility with great toughness. At present, the gutta percha is purified by rasping it in cold water, which removes the greater part of the soluble organic matter and salts, and also facilitates the separation of any portions of wood or earthy matters. The purification is completed by means of warm water in several basins; the gutta percha is afterwards dried, and formed into a pasty mass by heating it to about 230° F. in a vessel with a steam jacket.

The gutta percha thus prepared becomes sufficiently soft to be readily joined, stretched out into sheets or straps of any thickness, drawn into tubes of various diameters, and moulded into any form, whilst, on being slowly cooled, it acquires great tenacity and solidity. It is necessary however to remark, that the presence of a small quantity of water is sufficient to prevent the adhesion of its parts.

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Properties of common Gutta Percha.—The gutta percha, thus purified for manufacturing purposes, is of a reddish-brown colour; it readily becomes electrical by friction, and is a bad conductor of both electricity and heat. At the ordinary temperature of our climate, say from 32° to 77°, it possesses about as much tenacity as thick leather, with rather less flexibility; it softens and becomes sensibly doughy towards 120°, although still very tough. Its ductility is such at a temperature of from 110° to 141°, that it is readily extended into thin sheets, or drawn into threads or tubes; its flexibility and ductility diminish as the temperature becomes lower. It does not possess at any temperature the peculiar elastic extensibility which characterizes caoutchouc. Exposed for an hour to a temperature of 14°, its flexibility is slightly diminished.

In its various forms, gutta percha possesses a peculiar porosity, as may be shown in the following manner:—A drop of its solution in sulphuret of carbon is to be placed on a glass slip; the spontaneous evaporation soon reduces this solution to a whitish plate; if it be then examined with the microscope, the numerous cavities with which it is pierced may be distinctly perceived. These cavities may be rendered still more visible by means of a drop of water; the liquid gradually insinuates itself, the mass appears more opake, and by means of the microscope the cavities are seen to be enlarged.

Similar results are obtained by keeping immersed in water for a considerable time thin transparent laminæ, obtained by the evaporation by heat of a solution of gutta percha.

The preceding observations led me to think, that this substance retaining, in consequence of its porosity, a great many minute particles of air, owed to this circumstance its appearance of possessing a less density than that of water, namely 0·979. In fact, on stretching gutta percha under strong pressure, and immediately cutting the strips thus produced into very small pieces under water, the greater part of the fragments fell to the bottom of the vessel—some immediately, others after absorbing a certain quantity of water. The same result was also obtained by keeping very thin leaves of gutta percha, prepared by different methods, immersed for a month in water deprived of air; their pores becoming gradually filled with the liquid, they became heavier than the water, and then ceased to float. Gutta percha is also heavier in proportion to the length of time it has been exposed to the air, particularly in thin leaves.

The porous structure of gutta percha becomes changed into a fibrous texture when it is drawn out so as to double its length; then retaining but little extensibility, it supports, without breaking, the action of a force equal to double that required for its elongation in the first instance.

Common gutta percha resists cold water, damp, and also the various influences which excite fermentation; but it can be softened, and experience a sort of superficial doughy fusion by the action of the solar rays in summer.

It is not attacked by alkaline solutions, even when caustic and concentrated; ammonia, saline solutions, water containing carbonic acid, the various vegetable and mineral acids, do not act upon it;

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alcoholic liquors (wines, beer, &c.) do not touch it; even brandy scarcely dissolves a trace of it. Olive-oil does not appear to attack gutta percha when cold; when hot, it dissolves a small portion of it, which is again precipitated on cooling.

Sulphuric acid with 1 equiv. of water colours it brown, and disintegrates it with a sensible evolution of sulphurous acid.

Muriatic acid, in its saturated solution in water at a temperature of 68° F., attacks gutta percha slowly, and gives it a more or less deep brown colour, at length rendering it brittle.

Monohydrated nitric acid attacks it rapidly, with effervescence and an abundant evolution of fumes of hyponitrous acid; the substance is decomposed, and coloured of a brownish-orange red; it becomes doughy, and afterwards solidifies by degrees and remains friable.

In the cold, and even by heat, only a part of the gutta percha (0·15–0·22) is dissolved by anhydrous alcohol or æther. Benzine and spirits of turpentine dissolve it partially when cold, but nearly completely by heat. Sulphuret of carbon and chloroform dissolve gutta percha when cold; the solutions may be filtered beneath a bell-glass to prevent evaporation; the filter retains the foreign matters of a reddish-brown colour, whilst the solution passes perfectly clear and almost colourless. The filtered liquid, exposed to the air in a saucer, allows the solvent to escape, and deposits the white gutta percha in a plate of greater or less thickness, which shrinks gradually in proportion to the evaporation of the liquid.

Except the colour, which has disappeared, the gutta percha offers then the characters and properties mentioned above as belonging to the commercial substance. Submitted to a gradually-raised temperature, it softens and melts, and may be made to boil without acquiring a sensible colour; the transparent fluid gives abundant vapours, which are condensable into a nearly colourless oily liquid. The portions last distilled have a brownish-orange colour, and a thin layer of carbonaceous deposit remains adherent to the sides of the vessel.

Analysis.—We have said above that alcohol and æther can only dissolve a portion of gutta percha; this is because that substance consists, in fact, of three proximate principles, the separation of which has required very delicate observation, although they are very clearly distinguished by several of their properties*.

When gutta percha in thin leaves is brought into contact, in a close vessel, with 15–20 vols. of cold anhydrous alcohol, and the temperature raised slowly by means of the water-bath to the point of ebullition (172° F.), and kept at this point during several hours, the liquid, if filtered whilst boiling and left in a closed flask, will, at the end of from 12–36 hours, begin to deposit on the sides of the vessel and on the surface of the solution white opaline granules, distant from one another, but some of them in groups; their size will gradually increase for some days. These granules, carefully examined under the microscope, will be found to have the form of

* The author appears to be unacquainted with the researches of M. Arppe on this subject. See Chem. Gaz., vol. ix. p. 471.—Ed.

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spherules truncated by the sides of the vessel. Their surface is either smooth, or bristling with very small, transparent, elongated, lamellar crystals. Some superficial fissures appear to indicate that these spherules are formed of a sort of transparent yellow kernel covered with a white pellicle.

Such is really their singular crystalline structure, of which perhaps no other example is known. In fact, cold anhydrous alcohol dissolves the whole of the yellow, subjacent, spheroidal substance, whilst the superficial pellicles, in the interior of which the alcohol has substituted itself for the solid globule, appear whiter and less transparent.

The alcoholic solution, which has been for some days depositing this complex spheroidal crystallization, can again take up by heat a portion of the two proximate principles remaining in the substance, allowing a fresh quantity to crystallize on cooling. The extraction is completed by returning the boiling alcohol several times upon the gutta percha until it no longer dissolves anything.

The solid substance which has resisted the action of the solvent, possesses, with some modifications, the principal properties of crude gutta percha; we shall here call it *pure gutta* or *gutta*. As to the two other organic principles, one is a *yellow resin*, which is much more soluble in cold alcohol than the other, the *white crystalline resin*.

By taking advantage of these different degrees of solubility, we are enabled, with time and patience, to effect the complete purification of these three principles. The separation may also be effected by treating finely-divided gutta percha with cold æther, which dissolves the mixture of the two resins more abundantly than alcohol; they are afterwards separated from one another by the same treatment already described for alcohol.

The tendency of the white resin to form itself into groups of radiated lamellæ is manifested in a rather remarkable circumstance, which it is easy to reproduce. Narrow ribbons cut from a thin leaf of ordinary gutta percha are to be placed in a tube, and immersed in anhydrous alcohol. The tube is then closed, and left for twenty or thirty days, when a few whitish points appear here and there on the ribbons, and afterwards on the sides of the tube. These points, which become gradually larger, are formed of crystalline tufts of the white resin. Thus this proximate principle is separated directly, and in the cold, even when the atmospheric temperature is gradually rising, for instance during the spring or early summer.

The crystalline white resin, when completely purified by washings with alcohol, and then redissolved in anhydrous alcohol, is deposited by slow spontaneous evaporation in the air, in radiated lamellar crystals, forming sometimes symmetrical tufts arranged in stars, and then presenting the appearance of a sort of inflorescence.

Distinctive Characters and Properties of the Three Proximate Principles which constitute common Gutta Percha.

The most abundant of these three principles, forming at least from 75 to 82 per cent. of the whole mass, is the pure *gutta*, which presents the principal properties of the commercial substance; it is

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white, transparent at a temperature of 212° F., when all its parts are melted together; opake or semi-transparent when cold, from its then acquiring a structure which causes the interposition of air, or of a liquid possessing a different refraction from its own. This structure appears still more distinct than in the natural substance containing all three principles.

In thin sheets, and at a temperature of 50°–86° F., it is supple, tough, extensible, but not very elastic. At 112° F., it softens and turns back upon itself, and becomes more and more adhesive and translucent in proportion to the elevation of temperature, undergoing a sort of doughy fusion, which becomes more distinct towards 212°–230°. Heated beyond this point, it melts, boils and distils, furnishing a pyrogenous oil and carburetted gases.

Pure *gutta*, like the other two proximate principles, is quickly rendered electrical by friction, and is a bad conductor of heat; it generally floats on water, but sinks to the bottom as soon as its pores are filled with this liquid. It is insoluble in alcohol and æther, almost completely insoluble in benzine at 32° F.; it is soluble at 77°, and becomes more and more so in proportion as the temperature is raised. The saturated solution at 86° forms itself into a semi-transparent mass when cooled below 32°; alcohol precipitates the pure *gutta* from its solution in benzine.

At 32°, spirits of turpentine dissolves very little *gutta*, whilst it disintegrates and dissolves it readily when hot.

Chloroform and sulphuret of carbon dissolve the gutta in the cold.

After the extraction by means of æther of the two resins interposed in the thin leaves of white gutta percha, leaving the last portion of æther with which they were impregnated to evaporate in the open air, these leaves, enclosed in a flask, experienced, after remaining there for two months at a temperature of from 68° to 82° F., an alteration which appeared to depend on their porosity, the action of the air, and perhaps the æther retained in their pores. However it be, these leaves had then acquired new properties; they were brittle; exhaled a very distinct sharp odour; brought into contact with an excess of anhydrous æther, they were partially dissolved; the soluble portion, obtained by the evaporation of the æther and desiccation at 194° F., was glutinous and translucent; it became opake and hard by cooling down to 14° F.

Sulphuret of carbon, renewed three times in six days, and evaporated each time after two days' contact, left as residue a white flexible leaf. The portion not dissolved, swelled and transparent, did not appear to undergo any change when left in sulphuret of carbon for ten days.

This kind of spontaneous transformation would perhaps become complete if more prolonged; its study will require much time; it will perhaps put us in the way of ascertaining the causes of certain changes observed in some small objects formed of gutta percha. I have already been able to ascertain, that thin leaves, exposed for eight consecutive days to the action of the sun in moist air, were discoloured, and that their substance had become in great part soluble in æther.

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Monohydrated sulphuric acid disintegrates, and communicates a brown colour to the pure *gutta*, with evolution of sulphurous acid; after eight days' contact, the deep brown liquid, on dilution with water, becomes turbid, and furnishes a brown flocculent precipitate. *Nitric acid*, with a single equivalent of water, attacks the pure gutta with a lively effervescence, and the evolution of orange vapours of hyponitrous acid. *Muriatic acid*, in its saturated solution, slowly attacks the thin leaves of gutta, giving them a deep brown colour; at the end of eight days it becomes friable. The reaction of muriatic acid establishes an additional distinctive character between this proximate principle and the two others.

Crystalline White Resin, obtained pure by means of the operations above described; it presents itself as a light pulverulent mass, apparently opake, which under the microscope exhibits the transparent lamellar crystals. From 32°–212° F. it does not experience any sensible change; its fusion commences at 320°; at 347°–356° it acquires an oleiform fluidity and complete transparency, without any noticeable colour; it solidifies on cooling, shrinks, which causes it to split, and remains transparent and a little heavier than water.

The crystallized resin is very soluble in spirits of turpentine, in benzine, sulphuret of carbon, æther and chloroform; on the spontaneous evaporation of the two last solvents, it crystallizes in long, narrow, thin, pearly laminæ, forming separate groups radiating from common centres.

Anhydrous alcohol dissolves it pretty readily at the temperature of 167° F.; on cooling, groups of crystals separate, which increase during several days; the cold solution, decanted after crystallization, and left to spontaneous evaporation, yields similar crops of more voluminous lamellæ.

These crystals are not attacked or readily moistened by either cold or boiling water; as is also the case with hot or cold caustic alkaline solutions, ammonia, and the various dilute acids. Monohydrated sulphuric and nitric acids attack it, rapidly producing similar phænomena to those observed in their action upon pure gutta. Muriatic acid, on the contrary, does not act upon the white resin; in several of these characters it approaches to the breane extracted by M. Scribe from the resin of Icica*. It would be well to submit these two principles to a comparative study.

Yellow Resin.—This amorphous transparent resin, of a lemon or orange colour according to its thickness, is a little heavier than water, solid, and even hard and brittle, at 32° F.; it gradually becomes more flexible in proportion as the temperature is raised; at 122° F. it becomes pasty; it does not become completely fluid below 212° to 230°. Heated beyond this point, it boils, but then gradually undergoes considerable alteration, becomes brown, and evolves acid fumes and carburets of hydrogen.

This resin strongly retains the alcohol in which it has been dissolved; it is separated from it by heating *in vacuo* to 212° F. until bubbling entirely ceases.

* Chem. Gaz., vol. iv. p. 151.

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It is soluble in the cold in alcohol, æther, benzine, essential oil of turpentine, sulphuret of carbon and chloroform; all these liquids, when evaporated, leave as residue the amorphous resin.

Dilute acids, concentrated alkaline solutions, and ammonia do not attack the yellow resin. Monohydrated sulphuric and nitric acids act upon it rapidly, producing phænomena analogous to those exhibited with the other two principles. Muriatic acid, even in its saturated solution at 68° F., is without action upon it. But the most remarkable character of this resin is the power of forming, under the circumstances already indicated, those globose crystals covered with a white pellicle of another resin, and offering in their complex form the appearance of opaline spherules.

We see thus that the gutta percha, as it occurs in commerce, consists of three distinctly characterized proximate principles, besides some other matters in small quantities; the most abundant of these principles possesses the properties of the original substance; I give it the name of *pure gutta* or *gutta*; the two other principles are neutral resins.

In order to recal their characteristic properties, I will give the name of *crystalbane* or *albane* to that which is obtained without difficulty in white crystals; and that of *fluavile* to the third, which is yellow, and becomes sensibly fluid at a low temperature.

The commercial varieties which I have examined have given me the following proportions:—

Gutta	75	82
Albane	16	14
Fluavile.....	6	4

In the second part of this memoir I propose to indicate the elementary composition of these proximate principles, and the principal applications of the original substance.—*Comptes Rendus*, xxxv. 109.

On the Preparation of the Sulphate of Alumina.
By MM. Huria *and* Brunel.

Sulphate of ammonia and alumina is placed in shallow earthenware vessels in a drying furnace. When it has lost all its water of crystallization, it is powdered and placed in a cast-iron cylinder, one end of which is closed with an iron cover, which is luted air-tight. From the other end of the cylinder a bent cast-iron tube issues, which is connected with leaden tubes perforated with a number of holes, and lying horizontally in a wooden water-cistern lined with lead; the water must absorb the gas evolved. A safety-tube prevents the rising of the water into the cylinder.

The products of the decomposition of the sulphate of ammonia and alumina are now to be expelled at a cherry-red heat; the sulphate of alumina remains in the cylinder. The sulphite of ammonia that goes over serves again for the preparation of the alum, after being changed into sulphate of ammonia by oxidation in the air. The drying-furnace lies above the furnace in which the cylinder is heated to redness, and is heated by it.—*Bull. de la Soc. d'Encourag.*, 1852, p. 199.

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PATENT.

Patent granted to William Longmaid, *for Improvements in obtaining Gold.*

THIS invention consists in treating minerals containing gold in such manner that the quartz, or other minerals, are fused and become a fluid slag, when the gold is precipitated either by its density or by its affinity for iron. The minerals to be so treated may consist of quartz, limestone, clay, sand, iron pyrites, or other minerals which contain gold.

In carrying out the invention, the patentee first reduces the minerals to a size that will pass through a sieve of three or more holes to the inch. If the auriferous mineral be quartz only, he adds thereto such ferruginous, earthy, and alkaline substances as will produce a fluid slag when subjected to the action of heat in a reverberatory furnace: calcined pyrites, oxide of iron, lime, fluor spar, or any alkaline matters, are suitable ingredients for producing the necessary fusion; and the patentee has found that 50 parts by weight of oxide of iron, 50 parts of lime, and 100 parts of quartz form a good mixture. The mixed minerals are ground, in order to effect a perfect admixture thereof. The patentee states, that he prefers to select such minerals as are auriferous [for the purpose, we presume, of effecting the fusion of the auriferous mineral to be operated upon], when the same can readily be obtained, such as quartz, oxide of iron, lime, baryta, &c. A weighed quantity of the ground material, say 2 tons, is placed on the sole of a reverberatory furnace, and the door or hole in the roof, at which the charge is introduced, is closed. After the charge is well heated, it is stirred occasionally, which has the effect of rendering the slag more fluid. When the charge is well fused, if the gold existed in considerable quantity in the minerals under treatment, it will be mostly precipitated by reason of its density; but it will happen that a portion of the gold, and sometimes the entire quantity, will be retained in solution or suspension in the slag. When this occurs, metallic iron (old boiler-plate will be a convenient form) is put into the furnace, which has the effect of precipitating the gold upon its surface. The gold is separated from the iron by immersing the same, whilst red-hot, in molten lead; and the gold is afterwards extracted from the lead by the ordinary method of cupelling lead containing precious metals.

It is found advantageous to work a number of charges until a considerable quantity of gold has accumulated in the bottom of the furnace, taking care, when tapping off the slag from time to time, to leave sufficient to cover the gold. When it is necessary to withdraw the gold from the furnace, the bottom is fused as close as may be found convenient, and the remaining portion is taken out and broken up. The pulverized bottom is mixed with a suitable flux, and smelted in the manner above described for smelting the raw material. It is stated, that by this means any sensible loss of gold is prevented. —Sealed Jan. 30, 1852.

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THE CHEMICAL GAZETTE.

No. CCXXXIX.—October 1, 1852.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Chemical and Microscopical Examination of the Fabrics surrounding an Egyptian Mummy, and of certain Matters that were discovered whilst unrolling the same; with some Remarks on the Analysis of the Flesh of the Mummy, and on the Egyptian Method of Embalming. By* Messrs. WILLIAM *and* THORNTON J. HERAPATH†.

I. *Examination of the Wrappers or Bandages.*

THE first point to be determined was, of course, the nature of the materials of which the fabrics were composed, that is to say, whether they consisted of cotton or linen. Pieces of the cloth were accordingly subjected to the action of certain chemical reagents, as, for instance, a boiling solution of caustic potash, concentrated sulphuric acid, nitric acid, &c., a series of comparative experiments being at the same time made on cotton and linen. By these means we convinced ourselves that the bandages consisted entirely of the latter. These results were moreover confirmed by a microscopical examination, and are, we find, in strict accordance with those of former experimentalists.

We next proceeded to investigate the composition of the dye-stuff that had been employed in the manufacture of the outer sheet or envelope, which was stained of a dingy reddish-yellow colour‡. Here however we experienced considerable difficulty. The only facts that could be proved were,—1st, that the dye-stuff was undoubtedly of vegetable origin; and 2ndly, that no mordant had been employed to fix the colouring matter to the tissue of the cloth. The colouring matter itself, it was found, could be partly removed from the linen by simply digesting it in water, but more readily if the water was first rendered slightly alkaline by the addition of a little caustic potash or *liquor ammoniæ*. It was also bleached by an aqueous solution of chlorine.

* The mummy in question was deposited in the Bristol Institution, some years ago, by Mr. Thomas Garrard, the well-known antiquarian, and was recently unrolled under the superintendence of Mr. D. W. Nash, of Clifton. It was supposed to be about three thousand years old.

† Communicated by the Authors.

‡ The bandages themselves, we ascertained, were indebted for their peculiar yellow tint to the natural colouring matter of the flax-fibre, and not to a dyeing material, as was at first imagined.

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The absence of all mordants was proved by the fact, that neither alumina nor oxide of tin were contained in the ashes of the linen.

A few of the bandages, it should be observed, were marked with blue thread, which formed a small pattern, about half an inch broad, on the selvage ends. On subjecting this to a chemical examination, it was proved to have been dyed with indigo. This result agrees with that obtained by Mr. Thomson, in the case of a mummy that was unrolled several years ago*. As much controversy appears to have taken place on the subject, as to whether the blue threads that are usually met with in mummy-cloths were dyed prior or subsequently to the weaving of the linen fabrics containing them, we separated some of those from the selvages of the present specimen, and carefully examined them by means of a microscope. From the appearances they presented, we are induced to believe, that, in this instance, the former supposition is correct, and that the threads were dyed in the hank, by immersion either in the juice of the woad or a dilute solution of deoxidized(?) indigo. That the latter substance was employed for this purpose is far from improbable, for we know that the Egyptians were acquainted with the nature and uses of indigo, inasmuch as it is mentioned in the Periplus as one of the articles commonly exported from India to Egypt.

There is one fact connected with this branch of the subject, however, which is worthy of especial attention, both from the chemist and antiquarian. On examining some of the wrappers already alluded to, certain marks or hieroglyphical characters were observed indelibly fixed upon the linen. The letters were of a dark colour, and as well defined as if written with a modern pen. When these were cut out and incinerated, an ash was obtained, which yielded before the blowpipe, on charcoal, a globule of a white splendent metal, possessed of all the characters of silver. Hence it is clear that the Egyptians were acquainted with a marking fluid, analogous, if not identical in composition, to that in use at the present day†.

In the interstices between the bandages, &c., and in certain other places, were found congeries of minute delicate crystals, similar in appearance to sublimed benzoic acid or very pure naphthaline, one of which substances they evidently were. They were almost insoluble in water, and also in alcohol and æther when cold, but dissolved in the latter menstrua with facility on the application of heat. They were likewise very soluble in ammonia, and the solution on evaporation yielded fine plumose crystals, soluble in water. When the ammoniacal solution was evaporated to dryness, redissolved in water, and tested with a persalt of iron, it yielded a light fawn-coloured precipitate. The crystals, on examination by a lens of moderate power, were found to consist of fine, delicate, colourless plates, which fused and volatilized at a low heat. It is therefore

* *Vide* a paper "On the Fabrics surrounding Egyptian Mummies," Ann. der Chem. und Pharm., lxix. p. 128.

† *Vide* a letter "On Early Egyptian Chemistry," by William Herapath, in the July Number of the Philosophical Magazine.

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clear that they consisted of benzoic acid, and were doubtless formed by the action of heat on some of the balsamic or resinous materials that were employed in the embalming.

II. *Examination of the Flesh of the Mummy.*

The results of our experiments on the mummy-flesh agree in the main with those of former analysts, though we believe we have discovered one or two new facts that are not devoid of interest. We have found that the muscular fibre has not undergone the slightest decomposition during the many centuries that have elapsed since the time when the body was submitted to the skill of the Egyptian embalmers. By acting upon portions of the indurated muscle with water, alcohol, and wood-spirit successively, we have succeeded in purifying them from the resinoid and other matters that were used for their preservation, and have thus restored them to their original condition; by which means we have been enabled to ascertain the true colour of the skin of the ancient Egyptians.

A quantitative analysis of the flesh gave the following numbers:—

	In 100 parts.
Water	11·430
Peculiar dark brown-coloured substance, soluble in acidulated water when hot, but insoluble in cold water	8·010
Extractive matters soluble in water, with some acetate of soda and formiate of soda, &c.	30·656
Volatile oils	a little
Rich dark brown-coloured resinous matter, similar in appearance, &c. to myrrhine, soluble in boiling alcohol, and also in wood-spirit	17·000
Chloride of sodium	4·002
Sulphate of soda, with a little phosphate of potash	0·996
Fibrinous portion, insoluble in alcohol, water, æther and pyroxylic spirit:—Muscular fibre	26·274
Sand, silica, and gritty particles of earthy matter, with a little sulphate of lime	1·450
	100·000

The ashes of the flesh amounted to 8·328 per cent., and contained 1·880 parts of alkaline carbonates, principally carbonate of soda. The latter was evidently formed by the decomposition of the acetate and formiate of soda, &c., as not a trace of alkaline carbonate existed in the aqueous infusion of the flesh.

The points in our analyses to which we would direct particular attention are,—1st, the proof of the uniform distribution of the resinous matters throughout the substance of the flesh; 2nd, the detection of superacetate of soda in the aqueous infusion of the flesh; and 3rd and last, the discovery of formic acid.

The presence of resinous matters in the interior of the fleshy mass, and their uniform distribution throughout the muscular tissues, were demonstrated by carefully scraping off the external portions of

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a mass of flesh from the abdomen, powdering that which remained, and digesting it first in hot water, and subsequently in boiling wood-spirit. Upon evaporating the spirituous solution to dryness, a resinous mass was obtained exactly similar in character to that which was extracted from other parts of the flesh.

The presence of acetic and formic acids was proved in the following manner:—An infusion of the flesh was made by boiling a quantity of the powdered muscle in water, and filtering the solution. The dark brown filtrate thus obtained, which possessed a strong acid reaction, was carefully evaporated to dryness, and the residue introduced into a retort, where it was treated with an excess of dilute sulphuric acid, and the mixture heated to the boiling-point. The liquid which distilled over was strongly acid, and possessed the peculiar pungent smell which characterizes a mixture of acetic and formic acids. To this solution there was then added an excess of carbonate of silver, and the mixture was gently heated; effervescence took place, and a curdy precipitate was produced in consequence of the formation of chloride of silver. The latter, together with the excess of carbonate of silver, was then separated by filtration, and the filtered solution evaporated to dryness at a low temperature. A crystalline salt was thus obtained, which was only sparingly soluble in cold water. The aqueous solution of these crystals, when heated to the boiling-point, yielded a deposit of metallic silver, coating the interior of the vessel in which the operation was conducted. This was evidently caused by the decomposition of the formiate of silver. Upon decanting the solution from the silver deposit, and evaporating it to dryness, a salt was obtained crystallizing in fine silky needles. This was evidently acetate of silver. When purified by recrystallization, &c., it was found to contain 69·3 per cent. of oxide of silver; calculation requires 69·46 per cent.

From the facts just described, we are induced to believe, that in the process of mummification, a portion of the resin was introduced into the flesh in solution in soda, or rather carbonate of soda—natron,—with which substance we know the Egyptians were acquainted, and employed in the embalming of bodies; that the corpse was then dried, and afterwards subjected to certain other processes, amongst which, it would appear, we must include exposure to the vapours or fumes of pyroligneous acid. The latter, on being brought into contact with the resinate of soda, with which the body had been previously saturated, decomposed it; thus forming acetate of soda, and liberating the resin, which remained fixed in the tissues. A further application of heat then dispelled the excess of acetic acid, and at the same time served to render the incorporation of the resinous matters with the muscular fibre still more complete.

That acetic or pyroligneous acid was employed by the Egyptians in the preparation of the mummies is rendered very probable by the following passage that occurs in Pliny (Hist. Nat., lib. xvi. p. 2):—

"Pix liquida in Europa e teda coquitur, navalibus muniendis, multosque alios ad usus. Lignum ejus concisum, furnis, undique igne extra circumdato, fervet; primus sudor, aquæ modo, fluit

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canali; hoc, in Syria, cedrum vocatur, cui tanta est vis, ut in Ægypto, corpora hominum defunctorum, eo perfusa, serventur."

Now as it is clear, from a variety of circumstances, that heat was employed in the process, it is extremely probable that the acid was employed in the vaporous rather than the liquid state. The dark colour of the bandages in the immediate vicinity of the body, as well as the use of the sawdust in the abdominal cavity, would thus become intelligible on the supposition that the latter was employed, as an absorbent material, to hold the acid before the application of the heat; and that the former were stained by the resinoid and other matters dissolved by the acid as it was volatilized.

That the dark colour of the bandages just referred to is not occasioned by a partial destruction of the linen, in consequence of a too elevated temperature having been resorted to, but is owing rather to the presence of some dark-coloured substance analogous to extractive matter, was proved both by an ocular examination and the action of chemical tests.

The above suppositious explanation of the mummifying process is far more simple than any other that has been hitherto suggested, and moreover it is the only one which accords in every respect with the known facts.

The presence of formic acid in the mummy-flesh it is difficult to account for; and we are still undecided whether to ascribe it to its occurrence in some of the materials used in embalming, or to the spontaneous and partial decomposition of the muscular tissues, &c. of the body. That formic acid is produced, under certain circumstances, from some of the animal tissues, as for example by the action of oxidizing materials on muscular fibre, is well known; but it is still uncertain whether it was thus formed in the present instance. Future investigation will perhaps throw some additional light upon the matter.

III. *Examination of the Gilding.*

On the breast of the mummy, and concealed amongst the bandages, there was discovered a small waxen image of an insect, apparently the sacred *scarabæus*, the thorax and elytra of which were gilded with some metallic substance. Similar gilding was observed also on certain parts of the body of the mummy, as for instance on the penis, and around the aperture in the side which had been made for the removal of the viscera. It was hence interesting to determine the nature of the metal that had been employed for this purpose. On subjecting a small piece from the *scarabæus* to the action of nitric acid, it was found to be untouched by that solvent, though it was readily soluble in *aqua regia*, yielding a solution which, when tested before the blowpipe by Maughan's method, gave a purple metallic stain on the porcelain plate; and on examining by the microscope another piece of the gilding, which had been purified from all organic particles by treatment with boiling nitric acid, it was found to be of such extreme tenuity as to be to a certain extent permeable to light. From these experiments it appears that the

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gilding material was similar in constitution to the gold-leaf which is so much used in the arts at the present day, to which also it closely approximated, if it did not equal in delicacy*.

Mansion House, Old Park, Bristol,
September 19th, 1852.

On Albumen and Caseine. *By* N. Lieberkuhn.

The author has instituted an investigation of albumen and caseine, particularly with a view to the study of the relations of caseine and albumen to potash. The results of this investigation are as follows:—

If solution of albumen be treated with a concentrated solution of potash, there is produced, without the employment of heat, a gelatinous elastic substance, which possesses greater or less consistency according to the greater or less concentration of the solution of albumen; it is an albuminate of potash, from which the excess of free alkali can be removed by means of distilled water, although not without loss. The residuary substance is readily dissolved in boiling water and alcohol. The albuminates may be obtained in a sufficiently pure state for analysis from the neutral solutions. Its behaviour with reagents and solvents does not differ from that of the soluble caseine.

The caseate of potash is better prepared in an analogous state, if its alcoholic solution, obtained from perfectly fresh milk, be precipitated with æther, and the precipitate dried in the air. The same applies also to the albuminate of soda prepared from the blood, and the globulinate of soda from the crystalline lens.

As the albuminate of potash, by evaporation on the water-bath, becomes separated, by gradual decomposition, into potash and an insoluble skin of coagulated albumen, and the residue is nearly insoluble, so the corresponding combination of milk, by a similar treatment, also divides into alkali and an insoluble skin of coagulated caseine; and unless a particular solvent be present in the residue, only a trace of it can be dissolved in boiling water. The same is the case with perfectly fresh milk; when evaporated later, although still possessing a neutral reaction, a slightly acid, and apparently somewhat more soluble residue is left, the alcoholic or watery solution of which exhibits the same reactions as the soluble caseine described in the manuals of chemistry.

Exactly the same is the case with a substance which is obtained from the albuminate of potash by adding a little lactic or phosphoric acid to its solution, in such a manner that the precipitate formed disappears again, then evaporating, and extracting the slightly acid residue with boiling water. Soluble caseine in this form is there-

* According to Ehrenberg (see Pogg., xxiv. 40), the coloured transparency of gold does not become apparent until the thickness is reduced to the $\frac{1}{24,000}$dth of an inch. Commercial gold-leaf is said to be less than the $\frac{1}{280,000}$dth of an inch thick.

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fore a product of decomposition, and does not occur as such in the organism.

No albumen, or analogous form of free caseine coagulable by heat, can be shown to exist in milk; for—

1. The coagulable substance, discovered by Scherer, which behaves like albumen, is not only obtained by adding much lactic or acetic acid to fresh milk and heating the filtrate, but also from the similarly-prepared filtrate of boiled milk.

2. Boiled and evaporated milk, as well as fresh milk evaporated at 104° F., furnishes, by extraction with cold water, a fluid coagulable by boiling.

3. It cannot be maintained that the neutral serum, coagulable by heat, prepared by Quevenne, contains free albumen, because milk freshly drawn from the organism, evaporated on the water-bath at 212° F., and extracted with cold water, furnishes also a neutral coagulable fluid. Albuminate of potash, also, when chloride of calcium or chloride of barium has been previously added to its watery solution, becomes coagulated on boiling. The coagulability of a neutral fluid therefore is no proof of the presence of uncoagulated albumen.

4. Milk, treated according to Wurtz's method, never furnished traces of soluble albumen. The nitrogenous substance occurring in fresh milk exhibited the following forms,—one corresponding to the albuminate of potash, one coagulable by heat, and one separable by filtration from the serum.

In the investigations hitherto instituted, these three forms have been generally taken into consideration together. To decide whether albumen and caseine be identical, more exact determinations of the sulphur are required for the latter in its various forms, and also the explanation of what takes place during precipitation by rennet. Neither of the substances contains phosphorus.—Poggendorff's *Annalen*, lxxxvi. 117 and 298.

On the Amount of Water contained in the Tribasic Phosphate of Lime. *By* Dr. H. Ludwig.

If an aqueous solution of chloride of calcium mixed with ammonia be precipitated by an aqueous solution of sesqui-*c*-phosphate of soda, a slimy white precipitate is obtained, which shrivels up on the filter, and can then no longer be washed in the usual manner. If this opaline mass be taken from the filter and triturated in a porcelain dish, it again becomes fluid, and may then, by gradually increased pressure in linen, be freed from a great part of the adhering mother-liquor. If the phosphate of lime thus procured be again soaked with cold water, and again pressed, and this operation be repeated several times, a mass will be obtained, which in a damp state is of an opaline transparency, and a solution of which in nitric acid is not rendered in the least turbid by nitrate of silver. The washing is facilitated by drying the opaline mass at the ordinary temperature, reducing it to powder and treating it with cold water;

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it is then dried at the temperature of the air. The freshly-prepared air-dried precipitate contains in 100 parts—

CaO	41·20 =	84·0	40·87
cPO^5	34·79	72·0	35·04
HO	24·01	49·5	24·09

After the precipitate had been preserved for two years in an air-tight bottle, it had the following composition:—

CaO	44·34 =	84·0	44·8
PO^5	37·39	72·0	38·4
HO	5·20	9·0	4·8
HO	11·80	22·5	12·0

1 atom of water was driven off below 212°, the other above that temperature. It follows, therefore, from the above statements, that the ammoniacal solution of chloride of calcium, precipitated by an excess of sesqui-*c*-phosphate of soda, gives a precipitate, which, when well washed and dried at the ordinary temperature of the air, is constituted, when fresh, according to the formula 3CaO, cPO^5 + HO, 4½ water, but gradually loses water by keeping, and after two years consists of 3CaO, PO^5 + HO, 2½ water. The precipitate is free from chlorine, but contains a trace of ammonia even after two years' keeping. It is only partially soluble by long boiling in acetic acid, but readily in dilute nitric acid.—*Archiv der Pharm.*, vol. lxix. p. 286.

On Cod-Liver Oil. By M. Winckler.

According to some authors, cod-liver oil is a mixture of several proximate organic principles. The author controverts this opinion. According to him, cod-liver oil is an organic whole, which contains propyle, C^6H^7, instead of glycyle, C^6H^5. By the saponification of cod-liver oil with potash, he procured oleic and margaric acids. By the distillation of a mixture of 24 parts of cod-liver oil, 24 parts of water and 6 parts of caustic potash, frequently shaken up together during several days, and diluted before the distillation with 24 parts more water, he obtained oxide of propyle. By saponification with oxide of lead, he procured no glycerine, but oleic and margaric acids, and a new acid,—propylic acid.—Buchner's *N. Rep. f. Pharm.*, i. p. 165.

ANALYTICAL CHEMISTRY.

Contributions to Analytical Chemistry. By Wolcott Gibbs, M.D.

In an interesting memoir* on the analogy between the chemical relations of peroxide of lead and the so-called ozone, Schönbein has pointed out the remarkable fact that peroxide of lead precipitates

* Poggendorff's Annalen, lxxviii. 162.

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manganese completely from its solutions in hydrochloric and sulphuric acids, a compound of peroxide of lead and peroxide of manganese being formed. A portion of the lead is at the same time reduced to protoxide, and unites with the acid with which the manganese was combined. The oxidising action which takes place may be represented by the general equation—

$$PbO^2 + MnO \cdot XH = MnO^2 + PbX + HO.$$

Schönbein appears not to have remarked the importance of this observation in an analytical point of view. In investigating the subject carefully, I have been led to the conclusion that the peroxide of lead constitutes one of the most valuable reagents in analytical chemistry, since by means of it the oxide of manganese may be easily and completely separated from a number of other bases without the employment of ammoniacal salts. The use of ammonia, as is well known, frequently renders analyses conducted by the ordinary methods laborious and inaccurate, either from the number of operations involved, from the absorption of carbonic acid from the air, or from the unavoidable loss in driving off the ammoniacal salts by heat. The facts which I have determined, and which serve as the basis of the analytical applications of the peroxide of lead, are as follows:—

1. Peroxide of lead completely precipitates manganese from its neutral solutions in hydrochloric, sulphuric and nitric acids, slowly in the cold, but very rapidly by digestion or by boiling.

2. The presence of an excess of hydrochloric or sulphuric acid does not prevent the complete precipitation of the manganese; in these cases, however, chlorine or oxygen is set free, and the quantity of lead dissolved is greater than that which corresponds to the quantity of manganese precipitated. Such an excess of acid should be avoided as far as possible.

3. The presence of an excess of nitric acid prevents the precipitation of the manganese, since, as Crum long since showed, hypermanganic acid is formed, and remains in solution.

4. Tartaric acid, and those organic substances which are burned at the expense of the peroxide of lead, do not interfere with the precipitation of the manganese. The organic matter is first destroyed by the oxygen of the peroxide of lead, and afterward the manganese is precipitated by the excess of the peroxide added. When the quantity of organic matter present is large, it is always better to separate the manganese by means of hydrosulphate of ammonia in the usual manner.

5. When however oxalic acid is present, we may avoid the use either of an inconvenient quantity of peroxide of lead, or of hydrosulphate of ammonia, by means of chlorine or bromine. Either of these agents readily converts oxalates into carbonates by a well-known reaction, $RO, C^2O^3 + Br = RrB + 2CO^2$.

6. The presence of an excess of free acetic or succinic acid does not prevent the complete precipitation of manganese by peroxide of lead.

7. The same observation applies to the presence of sulphate,

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nitrate and chloride of ammonium, and therefore probably to all ammoniacal salts.

8. Salts of protoxide of iron are oxidized and partially precipitated by peroxide of lead.

9. The same remark applies to the salts of cobalt. The precipitation is not complete even after long digestion upon the sand-bath.

10. The salts of nickel and zinc are not precipitated by peroxide of lead, and the nickel undergoes no higher oxidation.

11. Peroxide of lead, when perfectly free from protoxide, does not precipitate baryta, strontia, lime, magnesia, or alumina from their solutions. The same remark applies, as might be supposed, *à fortiori*, to the alkaline bases. The application of these facts to the quantitative separation of manganese from the above-mentioned bases, with the exception of iron and cobalt, is obvious. The different cases deserve however to be considered separately.

Manganese from Potash and Soda.—Peroxide of lead is to be added to the neutral solution of the three bases in hydrochloric, nitric or sulphuric acid; the whole is then to be digested upon the sand-bath for an hour at a temperature of 85° C., care being taken to agitate the solution frequently and thoroughly with a glass rod. For every gramme of matter analysed, it is well to employ about 5 grammes of peroxide of lead. After digestion, the solution is to be filtered, and the mass upon the filter thoroughly washed with hot water. The filtrate contains the alkaline bases and lead, but is absolutely free from manganese. The lead is to be separated by means of a current of sulphuretted hydrogen, and in the filtrate from the sulphuret of lead the alkalies are to be determined in the usual manner; as there are no ammoniacal salts present, the estimation of the alkalies offers no difficulty when they are in the form of chlorides. When but a single alkali is present, its quantity may be determined by simple evaporation to dryness and ignition. The mass upon the filter, after washing, consists only of the peroxides of lead and manganese. The filter is to be dried, ignited gently in a porcelain crucible, and then heated with fuming nitric acid, which speedily produces a colourless solution. This is to be diluted sufficiently with water, and the lead separated by sulphuretted hydrogen. The filtrate from the sulphuret of lead contains only manganese, which may then be determined as usual by carbonate of soda. In the above process, it is almost always best to reduce the bases to be separated to the form of chlorides. The separation of the lead is much less easy when sulphates are present; while, on the other hand, the presence of nitric acid renders it difficult subsequently to determine the alkalies. When however but one alkali is present with manganese, we may employ a solution of the nitrates, since in this case the alkali, after the separation of the lead, may be estimated by fluosilicic acid and alcohol, as recommended by Rose. When the solution of the bases is acid, it may be neutralized with carbonate of lead; but this should be avoided if possible, since it is not desirable to introduce more lead into the solution than is absolutely necessary.

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When, as is generally the case in mineral analyses, iron is associated with manganese and the alkalies, it is most advantageous to peroxidize the iron by means of chlorine or bromine, and then to separate it from the other bases by means of carbonate of baryta. After the separation of the iron, the manganese may be separated from the alkalies by the methods above given, the presence of a salt of baryta not interfering in the process.

Separation of Manganese from Baryta, Strontia, Lime, Magnesia and Alumina.—The separation of manganese from these bases may be effected by the same process as that given above for its separation from the alkalies. When the alkalies are also present in the solution, all the bases should be, if possible, in the form of chlorides. When this is not the case, however, it is most convenient to employ the bases in the form of nitrates, avoiding the least excess of free nitric acid. After the digestion upon the sand-bath and before filtering, it is well to add a few drops of nitric acid when magnesia or alumina is present; the acid however should only be added after the solution has become nearly cold and when no alkalies are present. When iron is also present, but no alkalies, we may peroxidize and precipitate it by ammonia, and then separate the manganese from the filtrate by means of peroxide of lead. In this case, of course, the precipitated peroxide of iron also contains manganese, which must be separated in the usual manner. When however the alkalies are present, we may separate the iron and alumina by means of carbonate of baryta, and then determine the manganese as above, thus avoiding the presence of ammoniacal salts in the solution.

Separation of Manganese from Zinc and Nickel.—The processes to be followed in this case are the same as in the last. The addition of a few drops of nitric acid to the solution after digestion and cooling is advantageous, as the precipitation of a trace of zinc or nickel by any minute quantity of *protoxide* of lead which may be present is prevented. The peroxide of lead is a reagent of especial value for the separation of manganese from zinc, but is less serviceable where manganese is to be separated from nickel, since this metal is usually associated with cobalt. When cobalt and nickel are both to be separated from manganese, Ebelmen's method appears preferable to any other. From what has already been stated (8 and 9), it will be evident that the peroxide of lead cannot be employed to separate manganese from iron and cobalt. On the other hand, however, it is highly probable that this reagent will effect the perfect separation of manganese from glucina, zirconia, and the metals of the cerium group. But upon this point the writer cannot speak from actual experiment.

For the analysis of a mineral which contains silica, alumina, oxide of iron, manganese, lime, magnesia and the alkalies, I propose the following process, which appears *à priori* likely to prove advantageous. The silica is first to be separated in the usual manner by hydrochloric or hydrofluoric acid. The solution of the bases, after peroxidizing the iron, is to be treated with carbonate of baryta, to separate alumina and iron. To the filtrate from these bases peroxide

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of lead is to be added, to separate the manganese. The filtrate, after separating the lead by means of sulphuretted hydrogen, will then contain baryta, lime, magnesia and the alkalies, which are to be separated in the usual manner. By this method we may avoid in a great measure, if not entirely, the presence of ammoniacal salts, and obtain more accurate determinations of the lime and manganese than by the ordinary process.

As the investigations which form the subject of the present paper have been chiefly of a qualitative character, it was a matter of especial importance to the writer to possess a sufficiently delicate test for manganese. Crum's test offered of all others the greatest advantages; but as in the original paper in which this test is described it is simply stated that the reaction is a very delicate one, and as the circumstances which modify or prevent its process are not alluded to, it became necessary to make this point the subject of special study. The results obtained in this investigation are as follows:—

1. By means of Crum's test it is easy to detect the presence of the $\frac{1}{100,000}$th of manganese in a solution otherwise colourless. With proper care a much smaller quantity of the metal may be detected, but the above will form a good *practical* limit to the sensibility of the reaction.

2. The manganese in this reaction may be present as chloride, nitrate, sulphate or phosphate, without affecting the result.

3. The presence of sulphate or nitrate of ammonia, even in very large excess, does not sensibly affect the delicacy of the reaction.

4. The presence of chloride of ammonium in small quantity does not affect the reaction. When however the chloride is present in great excess, it is necessary to add a very large proportion of peroxide of lead, in order to obtain the characteristic rose or violet tint, as the lead is reduced to a chloride so long as there is sal-ammoniac in the solution. In this case, therefore, it is better to precipitate the suspected liquid by hydrosulphate of ammonia, and then to test the precipitate by nitric acid and peroxide of lead.

5. When organic substances are present, the solution should either be evaporated to dryness and ignited, or else precipitated by hydrosulphate of ammonia, and the precipitate tested. The first method would probably answer best in testing mineral waters.

6. The bases to be tested for manganese may be present as nitrates, sulphates or chlorides. In the latter case the characteristic violet or rose colour makes its appearance, even though chlorine is copiously evolved from the solution, on boiling with the nitric acid and peroxide of lead.

7. The presence of iron, even in large excess, does not very sensibly affect the delicacy of the reaction.

8. The presence of an excess of a salt of nickel completely prevents the reaction for manganese, the violet colour of the hypermanganic acid being lost in the green of the nickel compound.

9. The presence of a small excess of a salt of cobalt does not materially affect the reaction for manganese. It is however impossible, by the direct application of Crum's test, to detect the presence

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of a small quantity of manganese in a large quantity of a cobalt compound.

10. The difficulty which arises in the application of Crum's test when cobalt or nickel is present, may be completely avoided by the following process, which is based upon the observation of Maumené, that the colours of solutions of cobalt and nickel are complementary to each other. The solution of cobalt which is suspected to contain manganese is first to be freed as completely as possible from arsenic, copper and iron. To a portion of this solution contained in a test-tube, a solution of a pure salt of nickel is to be gradually added until the colour of the mixed fluid vanishes or becomes almost insensible. Nitric acid and peroxide of lead are then to be added, and the whole boiled for a few seconds, when the characteristic tint will appear if but a trace of manganese be present. The same process is to be applied in testing solutions of nickel for small quantities of manganese, a pure solution of cobalt being added till the original green colour of the solution is destroyed. It rarely happens, in the application of this method, that a perfectly colourless solution can be obtained; usually the mixed solution has a faint brown tinge, like that of commercial sulphuric acid. This tint however has no sensible influence on the result.

11. In all cases in which Crum's test is employed, the colour of the liquid must be observed immediately after boiling and subsidence of the excess of peroxide of lead, as the tint fades when the solution is exposed to air and light.

The constitution of the black substance which is precipitated from solutions of manganese by peroxide of lead has not yet been satisfactorily determined, in consequence of the difficulty of obtaining it perfectly free from an excess of peroxide of lead; and I propose to resume the subject in another paper. It appears, as stated by Schönbein, to be a chemical combination of the peroxides of lead and manganese; its chemical relations are as follows:—Hydrochloric acid readily dissolves it, even in the cold; the solution has a dirty brown colour, and evolves chlorine copiously on heating, becoming colourless. Red and fuming nitric acid gradually dissolves it with the aid of heat; ordinary nitric acid, nearly free from nitrous acid, dissolves but a very small portion, even after long digestion. Sulphuric acid has no action in the cold, but on heating evolves oxygen, while sulphate of lead is found. Oxalic and tartaric acids are readily oxidized by digestion with the black compound, with evolution of carbonic acid, and formation of carbonates of lead and manganese.

In another memoir I shall return to this subject, and give the results of quantitative analyses, conducted according to the methods pointed out in the present communication. It may be proper to state in conclusion, that the peroxide of lead employed in the above-mentioned investigations was obtained by the action of chlorine upon hydrate of protoxide of lead suspended in water. The resulting mixture of chloride and peroxide was thoroughly washed with boiling water to separate the chloride, and then repeatedly digested with nitric acid to remove every trace of protoxide of lead, washed and

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dried. As thus prepared, the peroxide is very dark brown, or nearly black; the commercial peroxide, which is prepared by the action of nitric acid upon minium, cannot be used either in qualitative or quantitative analysis, as it contains iron and manganese, as well as the other impurities of the minium employed.—Silliman's *Journal*, September 1852.

On the Quantitative Determination of Sulphur. By W. Heintz.

The author has employed the method followed by Bunsen for the determination of the relative proportions of nitrogen and carbon, in order to determine sulphur in a similar manner.

A wide combustion-tube is employed, drawn out at one end into a narrow tube in such a manner that the walls of this part of the tube may be as thick as possible. Into this tube the substance is introduced, mixed with only a little more oxide of copper than will exactly suffice for its complete combustion. The other end of the tube is then also to be drawn out in a similar manner into a narrow tube, and hydrogen gas allowed to pass through it until the atmospheric air is removed. Both ends of the tube are then hermetically closed. This tube is treated exactly as directed by Bunsen. It is laid in a cylindrical iron case, consisting of two halves, and filled with a mixture of plaster of Paris and finely-chopped cow's hair, and exposed in a proper furnace to a constant moderate heat. After the whole has again become cool, the tube is carefully cleaned from any adhering plaster of Paris, and then broken asunder; this is best effected by a scratch with a file. The contents of the tube are now to be thrown into a dish; the portion which cannot be detached from the tube is dissolved in a hot mixture of muriatic acid and chlorate of potash, and the solution also poured into the dish. The tube is to be rinsed with this mixture several times, after which the solution of the copper and oxide of copper in the dish is accelerated by heat. When this is completed and the solution is quite clear, which should be the case if the oxide of copper were pure, a very dilute solution of chloride of barium may be added to it, and the sulphuric acid precipitated as sulphate of baryta, which is weighed as usual. If the solution be not quite clear, it must be filtered, and only the filtrate precipitated by chloride of barium.

In this manner the author obtained from 0·2597 grm. of taurine, 0·483 grm. of sulphate of baryta. This corresponds with 0·0664 grm. or 25·57 per cent. of sulphur. Theory requires 25·60 per cent.

When it is necessary to employ large quantities of the substances, as is the case with the proteine substances, this process is inapplicable. In such cases the author proceeds as follows:—

A combustion-tube, about 3 or 4 feet long, is sealed at one end. About 12 inches from this end it is to be bent, without being sensibly narrowed, at an angle of about 90° or 100°. About 4 inches from this bend, the tube is to be again bent in the same manner, but in the opposite direction, so that the first and last portions of the tube may run in a direction nearly parallel. They must converge a

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little towards the mouth of the tube. This being done, the substance, weighed and mixed with oxide of copper, is poured into the tube. The tube is then inclined and tapped, so that the mixture may pass into that leg which is nearest to the sealed end. Oxide of copper is then poured in, until as much again has been introduced into the tube as is necessary for the combustion.

The open end of the tube is now drawn out into a narrow tube, and the substance and oxide of copper so arranged in the sealed leg that the latter may lie before the former, and that nearly the whole of this leg of the tube is occupied by them. Through the open end of the tube from 20–40 grms. of a tolerably strong solution of hydrate of potash are poured into it, in such a manner that this liquid may only moisten the longer leg of the tube. In this position the sealed end of the tube containing the substance is placed in a Liebig's furnace or over a combustion-lamp. The solution of potash is then washed out of the long leg of the tube by means of distilled water, the tube dried with blotting-paper and a gentle heat, and the narrowed portion bent down, without altering the position of the rest of the tube, so that the opening may be directed downwards. This opening is introduced into a beaker, so that it may be closed by a small quantity of solution of potash contained therein. The oxide of copper is brought to a red heat, and the mixture of oxide of copper with the organic substance then gradually heated. When the combustion is completed and the tube cooled, it is broken at the bend next the short leg, by throwing water on it whilst hot. The oxide of copper, the inside of the tube, and the solution of potash are now treated with the mixture of chlorate of potash and muriatic acid, in order to change any sulphurous acid into sulphuric acid, and the latter determined by chloride of barium.—Poggendorff's *Annalen*, lxxxvi. p. 424.

PROCEEDINGS OF SOCIETIES.

British Association for the Advancement of Science.—Meeting held at Belfast, September 1st, 1852.

On Irish Bog-Butter. By Mr. J. A. Brazier.

The substance bearing this name is found accidentally in the various boggy districts of Ireland, sometimes also in Scotland, and is usually preserved in small kegs, in which the matter had most probably been originally deposited. Nothing appears to be known as to what this substance formerly was, or the time of its deposit. The keg—the specimen supplying the material for my experiments—was found in this district, and was given me by my friend Dr. Andrews for the purpose of examination.

In Berzelius's Report for 1847, we find an examination of another

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specimen of this substance by M. Luck*, under the name of bogic acid, who describes it as a whitish substance, of low specific gravity, and of a peculiar odour. He fixes the fusing-point of the purified body at 124° F., describes its reaction towards litmus-paper as acid, and gives it the formula $C^{33} H^{33} O^4$.

The specimen at my disposal was of a yellowish-white colour, the slight tinge of yellow being owing to the presence of a very small quantity of a yellow oil pervading the whole mass, somewhat friable on the external surface; but portions of the interior of the mass had an unctuous feel and a most peculiar odour. It is nearly insoluble in cold water, somewhat soluble in hot, but very soluble in alcohol and æther, especially on boiling, from either of which fluids it is deposited in white granular crystals; the alcohol or æther separated from the crystalline deposit by expression was of a deep yellow colour, and contained apparently a small quantity of the oleaginous matter above mentioned in solution.

A clear portion of the substance, taken directly from the keg, gave a fusing-point of 113° F. after repeated crystallization from alcohol until the supernatant fluid no longer possessed the slightest yellow tinge when cold; and finally, once from æther, the fusing-point of the substance was raised to between 125°·6–127° F. This method of purification was repeated several times, the fusing-point of the body remaining constantly the same, the substance itself resembling after fusion ordinary stearic acid.

Before subjecting the substance to analysis, I thought it more advantageous to submit the body to a more rigorous method of purification, and adopted that of saponification. With potash this body forms a beautifully clear transparent soap, entirely soluble in water, with the exception of the small quantity of yellow oil which is seen floating on the surface of the solution, and is easily separated, together with other accidental impurities, by means of a separating-funnel or filtration.

The solution of the soap, on being decomposed by the addition of a small quantity of hydrochloric acid, deposits the fatty acid. This has to be well washed with large quantities of water, and subjected several times to considerable pressure. In this state the fusing-point was found to be 127°·4 F.; and the same portion of acid having undergone the same routine of purification a second time, the fusing-point was not altered. An analysis of the body thus purified furnished numbers corresponding to the formula $C^{32} H^{32} O^4$, and for which I propose the name of *butyro-limnodic acid*. The acid was subsequently recrystallized from alcohol, from which it was deposited, as usual, in granular crystals; from the ætherial solution however it was now deposited in crystals of a beautifully white satiny appearance, somewhat resembling benzoic acid. In this state the acid was carefully dried; its fusing-point was found to be the same as before, namely 127°·4 F., and upon analysis yielded numbers corresponding to the before-mentioned formula.

Having obtained a higher point of fusion than M. Luck for this

* See Chem. Gaz. for September 1845.—Ed.

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acid, and a less amount of carbon in the analysis, I am led to conclude that he could not have entirely removed the small quantity of oily matter, which he himself mentions is most tenaciously retained by the acid; and this being probably of the nature of a hydrocarbon, would tend naturally to increase the amount of carbon.

The products of this acid by oxidizing agents, I think, will be extremely interesting; from a few preliminary experiments upon it, I think it is likely to yield one or more of the fatty acids, lower in the scale of this series, viz. caproic, œnanthylic or butyric acid; but of this I can only vouch for the truth by the smell.

The kegs in which the butter was found are of the most primitive form of construction, and about 1 foot in height and 10 inches in diameter.

On the Influence of the Solar Radiations on the Vital Powers of Plants. By Dr. J. H. GLADSTONE.

The author set out by saying, that the question as to whether plants increase or diminish the amount of oxygen in the air, was long a matter of dispute. This arose, partly from the defective modes of analysing gases, experiments of plants being made under circumstances very unfavourable to their healthy development, and partly from the variations in light having a great influence in modifying the functions of the vegetable world. The history of these discussions he would not enter into. When it was fully conceded that carbonic acid really is decomposed by the plant, it was natural enough that those who observed that wonderful power of the chemical rays of the solar spectrum in reducing salts of silver and other substances, should refer the chemical changes taking place within the vegetable tissues to the same occult agency. But Dr. Daubeny has shown that it is the luminous, and not the chemical or calorific rays, which cause the decomposition of carbonic acid, with emission of oxygen from the leaves, the formation of chlorophyle, the irritability of the mimosa, the evolution of water, and directly, at least, the absorption of it by the roots. The colours of the flowers are also supposed, by this author, to depend also on the luminous rays; sunshine was found to act far more energetically than diffused daylight, while no effects were observed to be produced by any artificial illumination, not even by that afforded by incandescent lime. He then went on to refer to the influence of various atmospheric conditions in conjunction with light. This necessitated the employment of closed vessels, under which the plants should be grown; and glass was almost the only article, from its various properties, that could be employed. Bell-shaped glasses were procured, and they were made of various colours, in order that the various properties of the spectrum might be tested. The blue glass employed is of so intense a colour that it cuts off by far the greater portion of the luminous rays, but admits the chemical rays freely. The red glass, on the contrary, freely admits the calorific influence, but stops the chemical, whilst it diminishes the luminous power. Colourless glass was also employed. Hyacinths were chosen for the experi-

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ment, purple in colour and of the same size, healthy and beginning to put forth shoots. After some time being allowed them in that position, there was a great change in the several plants, which was evidently attributable to the quality of the light. First, as to the effects on the rootlets. Under the colourless glass they grew abundantly and very rapidly; under red glass scarcely any were produced, and never attained any great height; while under the yellow glass they were fine and long. In the other stages the same thing occurred, and the colours of the flowers all changed differently. Cereals were also grown in a similar way, and exhibited effects almost similar. The best plant was under the yellow light, and the worst under the blue light. One thing was observable, that the plants existed much longer from being in an unchanged position. The plants under the darkened shade of glass became sickly and died.

Analysis of a Substance resembling the Pigolite of Professor Johnston. *By* Professor APJOHN.

The learned Professor said he received it from a gentleman in Wicklow, and that it had been taken from a kind of rock. It was of different colours, and a little heavier than water. It was easily dissolved, but by the use of strong acids it might be brought back to its original state; and the experiments which he had made proved that it was of an acid nature. He then described the result of his analysation, which was that it was composed of 2 equivs. of an organic acid with 1 aluminous base. From his experiments it appeared to be identical with the Pigolite of Professor Johnston of Durham.

On the Detection of minute quantities of Soda by the action of Polarized Light. By Prof. ANDREWS.

The double chloride of potassium and platinum, crystallizing in regular octahedrons, exercises, when placed in the dark field of the polariscope, no depolarizing action; and the same remark applies to the bichloride of platinum, in consequence probably of its imperfect crystallization. On the other hand, the chloride of sodium and platinum in thin crystalline plates is remarkable for its depolarizing power; and a trace of this salt, which is invisible to the naked eye, may be at once detected by the brilliant display of prismatic colours which it exhibits under the action of polarized light. The author applies this property to the detection of soda in the following way:— The other bases having been removed by the ordinary methods, and the alkalies converted into chlorides, a drop of the solution is placed on a glass slide, and a very small quantity of a dilute solution of the bichloride of platinum added, avoiding as far as possible an excess of that reagent. The drop is then evaporated by a gentle heat till it begins to crystallize, and afterwards placed in the field of a microscope furnished with a good polarizing apparatus. On turning the analyser till the field becomes perfectly dark, and excluding carefully

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the entrance of light laterally, the crystals remain invisible if either potash, or no alkali whatever, be present, while the presence of the slightest trace of soda is at once indicated by the depolarizing action of its platinum compound. With a drop of solution of chloride of sodium weighing 0·0015 grm. and containing $\frac{1}{10,000}$dth of its weight of chloride of sodium, a very distinct effect was obtained. The quantity of soda thus detected was only $\frac{1}{13,000,000}$th of a gramme, or about $\frac{1}{1,000,000}$th of a grain.

On a new variety of Magnetic Iron Ore. *By* Prof. Andrews.

This mineral occurs in the schist rocks of the Mourne Mountains, near their junction with the granite. In external characters it resembles somewhat the common magnetic oxide, but its lustre is inferior. It occurs both in the amorphous state and in imperfectly-formed octahedrons. Its composition was found to be—

		Oxygen.
Sesquioxide of iron	71·41	21·42
Protoxide of iron	21·59	4·68
Magnesia	6·45	2·58

The formula of this mineral is evidently $Fe^2 O^3$ (FeO, MgO), a part of the protoxide of iron being replaced by magnesia. Although not mentioned in any of the published analyses of magnetic oxide of iron, magnesia appears to be a constant constituent of this mineral. The author gave the results of analyses of magnetic oxide, in which 2·00, 0·71, and 0·09 per cent. of magnesia had respectively replaced an equivalent amount of the protoxide of iron. It is remarkable that not a trace of lime could ever be detected in any specimen of magnetic oxide. Oxide of manganese is usually also present, but in very minute quantity. In this analysis a solution of the bicarbonate of baryta was employed to separate the sesquioxide of iron from the magnesia.

A solution of this kind, which is readily prepared by passing a current of carbonic acid into water containing recently-precipitated carbonate of baryta in suspension, the author finds to effect a very complete separation of the sesquioxide of iron from the oxide of manganese and from magnesia; and considers that it may be very usefully employed in quantitative analyses, presenting for the separation of the bases just mentioned many advantages over the insoluble carbonate of baryta, as well as over the other reagents usually employed for the same purpose.

On the Atomic Weights of Platinum and Barium.
By Prof. Andrews.

No determination of the atomic weight of platinum having been made since the recent revision of atomic weights, and the number adopted by chemists for that metal resting on the authority of a single experiment of Berzelius, the author considered it of importance, on practical as well as theoretical grounds, to institute some new experiments on the subject. The salt of platinum selected was the

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double chloride of potassium and platinum, which, after being dried *in vacuo* at a temperature of 105° C., was decomposed by digestion with metallic zinc and a small quantity of water, the action being assisted by the application of heat towards the end of the process. After the complete precipitation of the platinum, and the formation of chloride of zinc from the decomposition of the double salt, the excess of zinc was removed by the addition, first of acetic, and subsequently of nitric acid. The precipitated platinum was then removed by means of a small and carefully-washed filter, and the amount of chlorine in the solution of chloride of zinc ascertained by Gay-Lussac's process, which has been of late so successfully applied by Pelouze to the determination of several other atomic weights. The double chloride of potassium and platinum was found to retain $\frac{55}{10,000}$dths of its weight of moisture, even when dried at a temperature considerably superior to the boiling-point of water. In three experiments performed by this process the numbers obtained were 98·93, 98·84 and 99·06; the mean number, 98·94, expresses therefore the atomic weight of platinum.

For the atomic weight of barium the author obtained from two closely-accordant experiments the number 68·789; and concluded with some general observations as to the importance of a systematic series of experiments, to settle, if possible, definitively whether the law of Prout, that the atomic weights of all bodies are multiples of that of hydrogen, be universal. Dr. Andrews concluded by reading an interesting extract from a letter which he had received from Baron Liebig:—"It is not certain that Prout's law may not be true for oxygen, nitrogen and carbon, without it being necessary to assume, as a consequence, that other bodies behave similarly, that is, that their atomic weight must be exactly multiples by whole numbers of the atomic weight of hydrogen. The law is certainly not true of all bodies, but it may be true of certain groups, whose members, in respect to atomic weight, stand in a simple numerical relation to each other. The atomic weights of silicium, cobalt, strontium, tin, arsenic and lead, are in the same ratio as the numbers 1, 2, 3, 4, 5, 7. We do not see the necessity of this relation, but only the possibility. Why should fractional numbers only occur, and not whole also? I consider these relations only as facts; the law of the numbers themselves is quite unknown to us, as unknown as the absolute weights of the atoms."

Dr. Apjohn made some observations on the subject,—"Is mechanical power capable of being obtained by a given amount of caloric employed in the production of vapour, independent of the nature of the liquid?" He demonstrated, that, so far as power, expense, and danger were concerned, caloric could not be used in opposition to anything at present in use for the purpose of promoting power; and that the calculations of its efficacy were entirely an error, and that there would be a great loss of power proceeding from imperfect condensation.

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THE CHEMICAL GAZETTE.

No. CCXL.—October 15, 1852.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Stibmethylium and its Compounds. *By* H. S. LANDOLT.

In the author's last memoir upon stibmethyle*, it was shown, that by the action of iodide of methyle upon antimoniuret of potassium, there may be formed, not only stibmethyle, $StMe^3$, but also another substance, which was called stibmethylium, $StMe^4$, in combination with iodine; this iodide of stibmethylium being a compound of 1 atom of stibmethyle with 1 atom of iodide of methyle. It was shown that this stibmethylium behaves exactly like an organic radical, and is capable of forming with oxygen, sulphur, chlorine, iodine, acids, &c., compounds which agree perfectly with the corresponding combinations of potassium or ammonium. A more complete investigation of these compounds of stibmethylium is the object of the present memoir.

The material which served for the preparation of the compounds of stibmethylium was its iodide, which is obtained in the following manner:—A mixture of finely-powdered antimoniuret of potassium and quartz sand is treated with iodide of methyle. The iodide of methyle is readily obtained by the action of iodine and phosphorus upon wood-spirit. The wood-spirit must contain a little water, because otherwise the evolution of too much heat causes the loss of a large portion of iodide of methyle. If the flask be then allowed to stand, the iodide of methyle collects at the bottom; the supernatant liquid, which still contains wood-spirit, may be poured off, and again treated with iodine and phosphorus. The iodide of methyle is then distilled with water, and iodine added to the distillate as long as it produces discoloration. By repeated washings with water and rectification over chloride of calcium, the iodide of methyle is obtained pure. It is to be observed, that it is not necessary to employ perfectly pure iodide of methyle in the preparation of iodide of stibmethylium, the presence of a small quantity of xylite, acetone, &c. in the wood-spirit having practically no influence on the purity of the compounds of this substance. The iodide of methyle employed had the following composition:—

	Calculated.	Found.
Carbon	8·7	9·4
Hydrogen	2·2	2·3
Iodine	89·1	88·3

* Chem. Gaz., vol. ix. p. 181.

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The mixture of antimoniuret of potassium and sand is introduced into a flask, and a sufficient quantity of iodide of methyle poured over it to moisten the mass throughout. The flask, which always becomes more or less heated, is then united with the apparatus described by Löwig and Schweizer in their memoir on stibæthyle*, through which carbonic acid gas had previously been passed for a considerable time; the excess of iodide of methyle first goes over, and afterwards, when the flask is heated, stibmethyle. This operation is repeated with other flasks. In the receiver there are then two fluids; the lower is stibmethyle ($StMe^3$), the upper iodide of methyle (MeI); after a short time however they unite, and form iodide of stibmethylium ($StMe^4I$), in the form of a white, crystalline, often very hard mass. This is dissolved in warm water, the excess of iodide of methyle which is commonly present separated, and the solution set aside to evaporate slowly on the water-bath, when the iodide of stibmethylium crystallizes in remarkably beautiful large crystals.

Stibmethylium, StC^8H^{12}, or $StMe^4$.—The pure radical has not yet been prepared. In order to procure it, the following experiments, which however were interrupted by a deficiency of material, were undertaken. Finely-triturated iodide of stibmethylium was shaken up in a retort with an excess of powdered antimoniuret of potassium mixed with some quartz sand, during which the air was carefully excluded, as otherwise an explosion would have taken place. The flask was then connected with the same apparatus which was used in the preparation of the iodide of stibmethylium, and heated. Water first passed over, arising from the antimoniuret of potassium having attracted it during its pulverization; after this, on the heat being increased, an oily, slightly yellow fluid, which collected at the bottom of the receiver.

This oily product exhibited great affinity with stibmethyle. Like this, it was heavier than water, and appeared to be slightly soluble in that substance. When brought into contact with the air, it became immediately inflamed, with evolution of a white vapour, which on condensation gave a white powder slightly soluble in water. The solution had a faint alkaline reaction. The odour of this fluid was also perfectly similar to that of stibmethyle. The small quantity which was obtained was not sufficient for an elementary analysis.

From the analysis of the compounds of stibmethylium, that substance consists of—

Carbon	8 = 48		25·40
Hydrogen	12	12	6·35
Antimony	1	129	68·25

Compounds of Stibmethylium.—Stibmethylium exhibits the most perfect analogy possible with a metal, such as potassium or ammonium. It unites with 1 atom of sulphur, chlorine, bromine and iodine, and with 1 atom of oxygen furnishes a base, which in its alkaline properties holds a middle place between ammonia and pot-

* Chem. Gaz., vol. viii. pp. 201, 372.

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ash; this base forms with acids, neutral and acid salts, which in part appear even to be isomorphous with the corresponding salts of potash and ammonia. The distinction of the compounds of stibmethylium from those of potassium or ammonium is scarcely possible in the humid way. All these compounds, with the exception of the sulphuret, are inodorous; in water they are generally readily soluble, in alcohol less so, and in æther nearly insoluble; the double salt of chloride of stibmethylium and chloride of platinum is alone difficult of solution in all solvents. The compounds generally possess a bitter taste. Several of the salts contain water of crystallization, as, for instance, the neutral sulphate and the oxalate; the haloid salts are anhydrous; some attract water from the air and deliquesce, as the carbonate and oxalate.

The base can only be separated from the salts by means of potash or soda, which is known, because, when a glass rod moistened with muriatic acid is held over the surface of the fluid, white vapours are formed, the oxide of stibmethylium being somewhat volatile. Ammonia does not act; on the contrary, the ammonia appears to be separated from its salts by a solution of oxide of stibmethylium, for a glass rod moistened with muriatic acid held over such a fluid, produces much stronger fumes than over a solution of oxide of stibmethylium.

The behaviour of compounds of stibmethylium with reagents also agrees exactly with that of potassium compounds, for in none of them is the antimony to be detected by reagents; they must be completely destroyed before the properties of that substance come into notice. By the long-continued action only of sulphuretted hydrogen gas, a scanty precipitate of sulphuret of antimony is produced; and when dilute sulphuric acid is poured over zinc, and some salt of stibmethylium added to the mixture, the hydrogen evolved, being passed through a narrow aperture and set light to, produces a faint antimonial spot on a porcelain saucer held in the flame; but the antimony is undiscoverable by any other reagents, concentrated nitric acid even not excepted. Their bitter taste, and their behaviour when exposed to heat, are therefore nearly the only means of distinguishing the compounds of stibmethylium from those of potassium and ammonium.

The salts of stibmethylium are in general very constant; they may be exposed to a temperature of 212° to 284° F. without experiencing any change; but if they are long kept at this temperature, they appear to undergo decomposition, as an odour like that of stibmethyle becomes sensible. Except the carbonate, the iodide is in this respect one of the least constant compounds of stibmethylium. If this be several times recrystallized from water, it begins to smell, and a small quantity of a yellow substance, which is with difficulty soluble in water, is separated; this is probably iodide of stibmethyle ($StMe^3 I^2$). For this reason the analyses of this and of some other compounds, which were not prepared immediately from freshly-procured iodide of stibmethylium, do not agree so well.

If the salts be heated dry, they begin to emit an odour at 356°–392° F., and then take fire with a large white flame. If a glass tube

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closed at one end be employed, a white vapour is evolved, which partly condenses on the sides of the tube, but of which the greater portion immediately takes fire at the mouth of the tube.

With regard to the action of the salts of stibmethylium on the animal organism, some experiments were made in the Physiological Institute at Zurich, which showed that the antimony had entirely lost its action upon the organism, like the arsenic in the cacodyle compounds, which also stands in the most complete harmony with the fact, that in the compounds of stibmethylium the antimony is not discoverable by reagents. 5·4 grms. of a solution containing 2·1 per cent. of chloride of stibmethylium, and consequently about 2 grs., were injected into the jugular vein of a rabbit, without any remarkable symptom showing itself; the author himself afterwards took 2 grs. of chloride of stibmethylium dissolved in about 2 drms. of water without experiencing the least effect. 8 grs. of iodide of stibmethylium, given internally to a dog, also failed to produce vomiting. If this, or any other salt of stibmethylium, possess activity, it will no doubt be similar to that of the corresponding potash salt; at all events none of them exhibit emetic properties.

Oxide of Stibmethylium, $StMe^4O$.—If a watery solution of iodide of stibmethylium be treated with an excess of freshly-precipitated and well-washed oxide of silver, iodide of silver is instantaneously formed, and oxide of stibmethylium remains in the solution. It is then filtered quickly, and the solution evaporated under the air-pump with sulphuric acid, when a white crystalline mass remains, which is without doubt hydrate of the oxide of stibmethylium. This substance behaves in every respect like hydrate of potash; it is remarkably caustic, produces between the fingers the same slippery sensation as potash, and deliquesces when exposed to the air, attracting water and carbonic acid. It is readily soluble in water and alcohol; the watery solution possesses an alkaline smell and taste, and renders reddened litmus-paper blue instantly. If it be exposed to the air, it attracts carbonic acid, and then effervesces strongly with acids. If lime-water be added to the carbonate, a precipitate of carbonate of lime is produced, and the pure base again exists in the solution. Oxide of stibmethylium appears to be volatile in a small degree, for if a glass rod moistened with muriatic acid be held over a solution of it, white vapours are produced; nevertheless the solution may be repeatedly evaporated under the air-pump without any observable loss. If oxide of stibmethylium be heated in a test-tube, vapours are produced, which kindle in the air with separation of oxide of antimony and metallic antimony; by applying heat very cautiously, a portion of the base may be sublimed without decomposition.

The watery solution of the oxide of stibmethylium behaves in the following manner towards the solutions of various metallic salts:—

If solution of oxide of stibmethylium be added to the solution of an ammoniacal salt, ammonia is expelled without the application of heat.

Baryta, strontian, and lime are immediately precipitated from their solutions.

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With salts of magnesia and alumina, a white flocculent precipitate is produced.

With salts of oxide of chromium, a voluminous green precipitate results, which is soluble in an excess of oxide of stibmethylium, but may be again precipitated by boiling.

The oxides of iron are immediately separated from their solutions.

Protoxide of manganese is thrown down in the form of a white precipitate, which quickly becomes brown.

In salts of oxide of cobalt, a blue precipitate is formed, which afterwards acquires a green colour, and undergoes no further change by boiling.

Oxide of zinc is thrown down in the form of a white precipitate, which is soluble in an excess of the precipitant.

In the solution of a salt of the protoxide of tin, a voluminous white precipitate is formed, which acquires a brown colour by heat.

Chloride of platinum gives a yellow, sparingly soluble precipitate.

Oxide of lead is immediately precipitated.

Salts of copper give a precipitate of hydrate of oxide of copper, which is not soluble in an excess of oxide of stibmethylium.

Protoxide of mercury gives a black, peroxide of mercury a yellow precipitate.

In salts of silver, a brown precipitate is produced.

If a concentrated watery solution of oxide of stibmethylium be boiled with sulphur, a yellow fluid is obtained, from which, by the addition of diluted acids, milk of sulphur is separated with evolution of sulphuretted hydrogen.

If iodine be added in small quantities to a watery solution of oxide of stibmethylium and shaken, the iodine disappears, and a colourless fluid is obtained, which gives on evaporation crystals of iodide of stibmethylium. There is also separated a small quantity of a black, opake, thick fluid, which looks like melted iodine, is insoluble in water, and when heated, first gives off vapours of iodine, but then takes fire, leaving a residuum of iodide of antimony. It is only very gradually dissolved by solution of potash. It is possible that this substance is iodate of oxide of stibmethylium.

The composition of oxide of stibmethylium, derived from the analysis of its salts, is as follows:—

Carbon	8	48	24·37
Hydrogen	12	12	6·09
Antimony	1	129	65·48
Oxygen	1	8	4·06

[To be continued.]

On Butylic Alcohol. *By* A. Wurtz.

Every chemist who has rectified potato-oil knows that that liquid boils at a temperature considerably below 266° F. When the thermometer reaches this temperature, a considerable portion of the liquid has already distilled over.

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The distillate usually forms two layers, an inferior aqueous layer and a superior layer, which contains besides a certain quantity of amylic alcohol carried over, some common alcohol, and, as I have convinced myself, some butylic alcohol. These alcohols boil at different temperatures; they may therefore be separated by fractional distillations. In order to abridge these operations, which, as every one knows, are very tedious, I make use of a small globe-tube, surmounting the vessel in which the distillation is carried on, which allows the less volatile vapours to become condensed and fall back into the vessel.

In performing this distillation, it is observable that the thermometer remains stationary for a long time between 226° and 244° F. I collected separately the liquid which passes between these limits of temperature; and in order to get rid of the compound æthers which might be present, I boiled it for forty-eight hours with caustic potash. After fresh distillations, I collected separately the portion which passed about 234° F. It was butylic alcohol, as may be seen by the following analyses:—

	I.	II.	Calculation.
Carbon	64·55	64·49	8 = 64·86
Hydrogen	13·87	13·53	10 13·51
Oxygen	..	..	2 21·63

Butylic alcohol thus prepared is a colourless, strongly refractive liquid, of a less density than water. Its odour resembles that of amylic alcohol, except that it is less disagreeable and more vinous. Fusing potash changes it into butyric acid, with disengagement of pure hydrogen. Perchloride of phosphorus transforms it into chlorhydrobutylic æther.

When mixed with its volume of concentrated sulphuric acid, care being taken that the temperature is not raised, the liquid scarcely acquires any colour, and at the end of twenty-four hours it may be mixed with water without the separation of an oily stratum. If this liquid be saturated with carbonate of potash and evaporated to dryness on the water-bath, a mixture of sulphate and sulphobutylate of potash is obtained. It is easy to extract this latter salt by means of boiling absolute alcohol, from which it deposits on cooling in the form of brilliant laminæ. These crystals, which when dried possess a pearly lustre and an unctuous feel, contain no water of crystallization. Their composition is represented by the formula $\left.\begin{matrix} KO \\ C^8H^9O \end{matrix}\right\} 2SO^3$, as may be seen from the following analyses:—

Carbon	24·82	..	8 =	24·97
Hydrogen	4·94	..	9	4·68
Oxygen	..	..	1	
Sulphuric acid....	..	..	2	
Potash	..	24·11	1	24·55

The sulphobutylate of potash was distilled on the oil-bath with cyanate of potash. There passed over into the receiver a liquid containing a mixture of butylocyanic and butylocyanuric æthers. This

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mixture, decomposed by potash, furnished an ammoniacal product of distillation containing butylamine. By saturating this with muriatic acid, muriate of butylamine was obtained, with which the double salt of platinum was formed.

The double muriate of butylamine and platinum forms beautiful spangles of a golden-yellow colour, which are soluble in absolute alcohol, and contain 35 per cent. of platinum. The formula $C^8 H^{11} N, HCl, PtCl^2$ requires 35·3 per cent. of platinum.

The reaction which I have just described, by furnishing us with the means of preparing a large quantity of butylamine, will permit us to decide whether this base and the *petinine* of Anderson are really identical, or only isomerous. Petinine might, in fact, be identical with the biæthylamine of Hofmann—

$$C^8 H^{11} N = \left\{ \begin{matrix} C^8 H^9 \\ H \\ H \end{matrix} \right\} N = \left\{ \begin{matrix} C^4 H^5 \\ C^4 H^5 \\ H \end{matrix} \right\} N.$$

Butylamine. Biæthylamine.

It is clear that the liquid which I have found in potato-oil is characterized in the most distinct manner by its general properties, and ranges itself in the series of alcohols. As soon as I have obtained a sufficient quantity in a pure state, I will ascertain whether, like amylic alcohol, butylic alcohol possesses the property of deviating the plane of polarization.—*Comptes Rendus*, Aug. 30, 1852, p. 310.

Note on the Commercial Analysis of the Cyanide of Potassium.

By M. J. Fordos *and* A. Gelis.

The cyanide of potassium, as manufactured for industrial purposes, is an extremely impure substance, containing scarcely half its weight of the actual cyanide. Its form, which is that of a melted mass, exposes it, more than any other substance, to adulteration; and yet nothing has been done by chemists with the view of discovering the means of readily ascertaining its commercial value.

Nevertheless the industrial importance of cyanide of potassium is becoming greater every day, and the extent of its consumption for galvano-plastic and photographic purposes is already sufficiently important to render this omission of chemists a matter of regret. For this reason we have sought to repair it.

The analytical process which we propose, but into the details of which we cannot enter here, is founded upon the action exercised upon cyanide of potassium by iodine. These two bodies combine rapidly with one another, every equivalent of cyanide of potassium absorbing exactly 2 equivs. of iodine.

The nature of the products thus formed is perfectly well known, and the reaction, which is represented by the formula—

$$CyK + 2I = IK + ICy,$$

has been studied by Serullas and Wöhler. The two components of the cyanide of potassium divide the iodine exactly between them, and the result is 1 equiv. of iodide of potassium and 1 equiv. of iodide of cyanogen.

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Knowing the reaction, it remained for us to determine the conditions under which it ought to be produced for the purpose proposed, and to indicate the precautions required in the operation: this we have done in our detailed memoir.

It was necessary also to guard against the action which might be exercised upon the iodine by the foreign substances which are found in commercial cyanides, and which have been added to it by design. We attained this result by the employment of Selzer-water in our analysis; the carbonic acid contained in it change the caustic alkalies and the carbonate of potash into compound bicarbonates, which do not absorb iodine.

We have made numerous trials of this process, and we have succeeded, by means of the indications which they have furnished us, in modifying the processes hitherto employed in the preparation of cyanide of potassium, and which could only give impure results.—*Comptes Rendus*, August 1852, p. 224.

On some Molybdates, and the application of Molybdic Acid for the Determination of Phosphoric Acid. By M. SONNENSCHEIN.

The author has prepared and examined a series of compounds of molybdic acid with ammonia and various metallic oxides, and among others that with oxide of copper is especially characterized by its forming well-defined crystals.

Ammonio-molybdate of Oxide of Copper.—This salt is prepared by digesting molybdate of ammonia containing an excess of ammonia with fresh-precipitated oxide of copper. When there is an excess of molybdate of ammonia present, a salt is formed in small prismatic crystals, which were not further examined. In the contrary case, measurable crystals—four-sided prisms—of a fine blue colour separate on evaporation, which, when exposed to the air, soon lose their brilliancy and become yellowish-green. This change is owing to loss of ammonia, which however does not amount to more than one-half of the entire quantity in the salt. It does not dissolve in water or alcohol, but is decomposed with separation of ammonia. On the contrary, it dissolves in ammonia and dilute acids. It is almost entirely soluble in sulphuret of ammonium, probably in consequence of the formation of a sulphur salt of copper and molybdenum soluble in sulphuret of ammonium. For this reason, in the analysis of this salt, the copper cannot be separated in the ordinary manner by this reagent.

The examination of this salt was carried out in the following way:—The quantity of ammonia and water was estimated from the loss on ignition; the quantity of oxide of copper by melting with carbonate of soda. The molybdic acid was precipitated from the solution by means of protonitrate of mercury, and ignited with a known quantity of oxide of lead. In order to determine the ammonia directly, another quantity of the salt was ignited with potash in a suitable apparatus, and the ammonia collected in hydrochloric acid weighed as ammonio-chloride of platinum.

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The analyses gave with the first-prepared salt the following results:—

		Calculated.	I.	II.	III.
Oxide of copper ..	495·6	27·09	27·31	26·97	27·30
Molybdic acid....	896·1	48·92	49·81	48·98	48·01
Ammonia.....	212·5	11·61	11·70	11·51	11·95
Water	224·96	12·29	12·00	11·92	12·23

The formula is therefore $CuOMo, NH^3 + 2HO$.

Ammonio-molybdate of Cobalt.—This compound is prepared in the same way as the former, with the exception that more care must be taken to have an excess of ammonia, so as to prevent the separation of an insoluble salt. The thin prismatic crystals of this salt cannot be measured. They are of a red colour, and consist of $CoO\ MO^3, NH^3 + HO$. They gave on analysis,—

		Calculated.	I.	II.	III.
Oxide of cobalt..	468·65	27·74	27·52	28·01	27·12
Molybdic acid ..	..	53·03	52·84	53·42	52·90
Ammonia	..	12·57	11·99	12·46	12·78
Water.....	..	6·66	6·48	6·73	6·58

Ammonio-molybdate of Nickel.—The preparation of this salt, and its behaviour when exposed to the air, are precisely the same as those of the previously-mentioned compounds. It is decomposed by water into a salt containing a larger quantity of water, which dissolves, and one containing less, which is insoluble. The composition is—

		Calculated.	I.	II.	III.
Oxide of nickel..	469·33	27·77	27·21	27·10	26·93
Molybdic acid ..	..	53·01	53·02	52·91	52·82
Ammonia	..	12·57	12·40	12·19	12·61
Water.....	..	6·65	6·11	6·50	6·65

The formula is therefore $NiO\ MO^3, NH^3 + HO$.

Ammonio-molybdate of Zinc.—Prepared as above. The salt forms small crystals of a silky lustre, which cannot be measured. It contains—

		Calculated.	I.	II.	III.
Oxide of zinc....	506·59	29·32	28·94	29·05	28·83
Molybdic acid ..	..	51·87	51·80	51·23	50·99
Ammonia	..	12·30	11·98	12·12	12·05
Water.....	..	6·51	6·16	6·24	6·02

Formula, $ZnO\ MO^3, NH^3 + HO$.

Ammonio-molybdate of Magnesia.—Prepared as above. The crystals cannot be measured, are transparent when fresh, and become opake on keeping. They contain in 100 parts—

		Calculated.	I.	II.	III.
Magnesia	258·14	17·45	16·81	16·51	16·15
Molybdic acid ..	..	60·58	60·10	61·00	60·21
Ammonia	..	14·37	14·07	13·84	14·11
Water.....	..	7·60	7·62	7·31	7·02

Formula, $MgO\ MO^3, NH^3 + HO$.

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Behaviour of Molybdic Acid towards Phosphoric Acid.—Sonnenschein has repeatedly examined the yellow precipitate produced in phosphates by molybdate of ammonia, and has come to the conclusion, that the phosphoric acid which it contains is an essential constituent, and not, as Struve and Svanberg suppose, an accidental admixture.

He prepared this compound thus:—To a solution of molybdic acid mixed with excess of ammonia he added $\frac{1}{10}$th of *c*-phosphate of soda, and then nitric acid in excess. The analysis of the precipitate which was formed immediately was conducted in the following manner:—The substance, dried at 218°, was ignited in a platinum crucible, moistened with nitric acid, and again ignited until there was no longer any loss of weight. From another quantity, dissolved in water, the phosphoric acid was precipitated by magnesia, and then the molybdic acid by protonitrate of mercury. The following three results are selected from a large series of analyses:—

	I.	II.	III.
Molybdate of ammonia and water..	11·23	10·91	11·40
Phosphoric acid.....	3·02	2·93	3·12
Molybdic acid	86·70	86·11	85·42

When this precipitate is long washed with dilute nitric acid containing a little molybdate of ammonia, the quantity of phosphoric acid is not in the least altered. Moreover, the presence of an ammoniacal salt is necessary to the formation of this compound. As the molybdate of ammonia is such a delicate reagent for phosphoric acid, Sonnenschein has examined the action of other substances upon the precipitate, and found that it is

Soluble in—	Insoluble in—
A large quantity of water.	Molybdate of ammonia.
A large quantity of alcohol.	Nitric acid.
Caustic and carbonated alkalies.	Hydrochloric acid.
a-, *b*-, *c*-phosphate of potash, soda and ammonia.	Dilute sulphuric acid.
Biborate of soda.	Sulphate of soda, potash and ammonia.
Hyposulphate of soda.	Bitartrate of potash.
Hyposulphite of soda.	Binoxalate of potash.
Acetate of soda.	Chloride of potassium.
Arseniate of soda.	Iodide of potassium.
Tartrate of potash and soda.	Bromide of potassium.
Oxalate of ammonia.	Bromide of sodium.
Phosphoric acid.	Nitrate of potash.
Concentrated sulphuric acid.	Nitrate of soda.
	Chlorate of potash.
	Boracic acid.
	Tartaric acid.
	Oxalic acid.

It is worthy of remark, that at a high temperature, 212°, arsenic acid likewise causes a yellow precipitate in molybdate of ammonia, which contains 7 per cent. of arsenic acid, and in its behaviour towards reagents closely resembles the compound containing

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phosphoric acid. Since now at the ordinary temperature no precipitate is caused by arsenic acid, and the ammonio-molybdate of magnesia is a very soluble double salt, arsenic may be quantitatively separated from molybdenum by this means. It is only necessary to convert both metals into acids, to precipitate their ammoniacal solutions by magnesia, and to determine the ammonio-arseniate of magnesia in the usual way.

In order to employ molybdic acid for the quantitative determination of phosphoric acid, Sonnenschein proceeds in the following manner:—He makes a solution of 1 part molybdic acid, 8 parts ammonia and 20 parts nitric acid, and adds as much of this to a solution of phosphate in nitric acid as is sufficient to make the quantity of molybdic acid in the mixture 30 times as great as the phosphoric acid. The liquid and the yellow precipitate are digested for some hours at a gentle heat, and then the precipitate washed out with the liquid used to produce it. The precipitate is then dissolved from the filter by ammonia, and phosphoric acid precipitated from the liquid by a magnesia salt.

As proofs of the applicability of this method, the analyses of artificial mixtures are given, as well as of a specimen of wavellite from Allendorff, from which a quantity of phosphoric acid was obtained by this process almost exactly corresponding with the calculated quantity.

1. 1·765 gr. $2NaO, HO\,PO^5 + 24HO$ gave—

		Calculated.
NaO	0·307	0·306
PO^5	0·350	0·351
HO	1·106	1·108

2. 1·234 gr. $2MgO\,PO^5$ gave—

MgO	0·45	0·452
PO^5	0·779	0·781

3. 0·948 gr. $Fe^2\,O^3\,PO^5$ gave—

$Fe^2\,O^3$	0·500	0·501
PO^5	0·444	0·446

4. 1·041 gr. $Al^2\,O^3\,PO^5$ gave—

$Al^2\,O^3$	0·435	0·435
PO^5	0·605	0·605

5. 0·852 gr. $3CaO, PO^5$ gave—

CaO	0·449	0·450
PO^5	0·380	0·381

6. 0·213 gr. $3CaO, PO^5 + 0·31\ Al^2\,O^3\,PO^5 + 0·231\ 2MgO, PO^5 + 0·560\ Fe^2\,O^3, PO^5$ gave—

CaO	0·113	0·116
$Al^2\,O^3$	0·127	0·130
MgO	0·084	0·085
$Fe^2\,O^3$	0·295	0·297
PO^5	0·679	0·686

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100 parts of wavellite contained—

Al^3O^3	35·76
CaO	0·86
PO^5	32·16
SiO^3	2·70
HO	28·32
Fe	trace

Finally, it must be remarked, that *a*- and *b*-phosphoric acids are not precipitated by molybdate of ammonia, at least the precipitation does not take place until they have been converted into *c*-phosphoric acid.—*Journ. für Prakt. Chem.*, vol. liii. p. 399.

PROCEEDINGS OF SOCIETIES.

British Association for the Advancement of Science.—Meeting held at Belfast, September 1st, 1852.

On the Estimation of Iodine. By Dr. Frederick Penny, *Professor of Chemistry, Andersonian University, Glasgow.*

Among the many applications that may be made of bichromate of potash to the purposes of centigrade analysis, there is none more convenient or useful than its employment for the estimation of the amount of iodine in samples of commercial iodine and of iodide of potassium. In Glasgow especially, which is the principal focus of the manufacture of salts of potash, and of iodine from kelp, and where the problems referred to are frequently presented for solution, an expeditious and exact method for the determination of iodine becomes truly valuable.

According to the statements of a party well qualified to judge, it appears, that, in the kelp season of 1851, the total quantity of kelp brought to Glasgow was about 6000 tons (22½ cwt. to the ton), which may be considered a fair average of ordinary seasons. On account of the greatly increased demand for potash-salts, the arrivals in 1850 amounted to nearly 10,000 tons, which is considerably higher than for several previous years*. The manufacture however is not confined to Glasgow; there are iodine works at Borrowstowness,

* *Kelp Imports in Glasgow. July to July.*

1841–42	2565 tons.
1842–43	1887 ...
1843–44	1965 ...
1844–45	3263 ...
1845–46	6086 ...
1846–47	3627 ...

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Greenock, and Falkirk, in Scotland, at Ramelton in Ireland, and at Cherbourg and Brest in France.

The centigrade process, here to be described, for the estimation of iodine, is based upon the fact, that chromic acid in presence of hydrochloric acid causes the complete decomposition of soluble metallic iodides, the chloride of chrominm and the chloride of the other metal being produced, while the iodine is thrown down in the solid state. Bichromate of potash is taken as the most convenient and stable form of chromic acid. The reaction with iodide of potassium is exhibited in the following equation:—

$$3KI + KO, 2CrO^3 + 7HCl = I^3 + 4KCl + Cr^2Cl^3 + 7HO.$$

The action is immediate, and provided that the solutions are kept cool, no secondary result is formed. The precipitated iodine speedily subsides, leaving the supernatant liquid quite clear, though slightly coloured, with a few floating particles of iodine on the surface. When the solution of the bichromate is overdosed with the iodide, it becomes dark red, from a portion of the iodine being dissolved by the excess of the iodide. This change of colour is useful as indicating when the addition of the iodide has been carried too far.

Iodide of Potassium.

The process for iodide of potassium is conducted as follows:—

10 grs. of bichromate of potash are dissolved in $\frac{1}{2}$ an ounce of cold water, and $\frac{1}{4}$ of an ounce by measure of hydrochloric acid is afterwards poured in.

An alkalimeter of 100 measures is then made up in the usual manner with 50 grs. of the iodide of potassium dissolved in water, and the solution is added to that of the bichromate of potash until the chromic acid is completely decomposed. To hit the exact point at which the action is complete, a white plate is spotted with a solution containing a mixture of pure protosulphate of iron and sulphocyanide of potassium, slightly acidified with hydrochloric acid, and by means of a glass rod a small quantity of the bichromate liquor is brought into contact with the mixture on the plate. So long as a red colour, or even dark tinge, is communicated to the spots by the application of this test, the presence of chromic acid is indicated; but when no dark shade is produced, the action is complete, and the operation is finished. The number of measures used is accurately read off, and the per-centage quantity of iodine in the sample subjected to trial is found by dividing 5080 by this number, 10 grs. of bichromate being equal (as will presently be shown) to 25·4 of iodine, and to 33·3 of iodide of potassium.

Throughout the process the liquid should be kept quite cool, and towards the conclusion the iodide solution in the alkalimeter should be added very slowly, in order to give ample time for the mutual action of the iodide and chromic acid, which should likewise be assisted by repeated and brisk stirring.

The mode of preparing the mixture of protosulphate of iron and sulphocyanide of potassium, as well as its extreme delicacy in de-

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tecting minute quantities of bichromate of potash, I have fully explained in a paper published in the 'Quarterly Journal of the Chemical Society of London,' vol. iv. 244. It should be made very weak, and in using it the precaution should be observed of not spotting it on the plate until the moment of its being required. The spots moreover should be large, and thinly spread on the surface of the plate, and care should be taken to bring the drop of the liquor to be tested into contact with the centre of the spot, which it is allowed merely to touch, without any stirring or agitation. The colour or tinge is produced instantaneously if any chromic acid be present. It is not always easy to procure protosulphate of iron perfectly free from peroxide, and then the mixture prepared with such impure sulphate has a pinkish colour. This is of no moment when the tinge is light, as it becomes extremely pale and scarcely perceptible on the mixture being spread upon the plate. In the case of the mixture, however, being dark coloured from the impurity of the sulphate of iron, it is better to dissolve a small piece of iron wire in dilute hydrochloric acid, and to add a portion of the clear solution at once to the sulphocyanide of potassium previously dissolved in water.

When minute accuracy is required, it will be advisable to add 30 grs. of the iodide, dissolved in a small quantity of water, at once to the bichromate solution; then to make up the alkalimeter with 10 or 20 grs. of the iodide, and to proceed with the operation as before directed. By using in this way a very weak solution of the iodide, it is perfectly easy to bring the result within a tenth of a grain of the proper quantity.

I have tried this process repeatedly upon carefully-purified iodide of potassium, both in large and small quantities. The results, which never differed more than a tenth of a grain from each other, show that 160 parts of bichromate of potash are equal to 333 of iodide of potassium, and to 254 of iodine; and accordingly 10 grs. of bichromate are equivalent to 25·4 grs. of iodine.

The following are some of the results obtained by subjecting different specimens of commercial iodide of potassium to trial by this process:—

Samples.	Iodide of potassium.
No. 1.	99·8 per cent.
2.	99·5 ...
3.	93·6 ...
4.	88·8 ...
5.	79·3 ...
6.	30·2 ..

The last sample consisted chiefly of carbonate of potash.

Iodine.

When iodine is the subject of examination, it must be first converted into a soluble iodide. The iodide of zinc appears to be best adapted for the purpose, from its stability and the readiness with which it may be prepared. 50 grs. of the iodine to be tested are

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put into a small flask with some fragments of pure zinc and half an ounce of water. The mixture is agitated till the iodine becomes completely converted into iodide of zinc, which is indicated by the solution losing the dark red colour that it first acquires, and becoming nearly colourless. The solution is then decanted into an alkalimeter, which is made up to 0 with rinsings from the excess of zinc.

10 grs. of bichromate of potash are next dissolved in a small basin with half an ounce of water, and a quarter of an ounce of hydrochloric acid is subsequently added.

The remaining operations are precisely similar to those directed for iodide of potassium. The iodide solution is dropped into that of the bichromate till no coloration is produced with the sulphocyanide mixture; then 5080, divided by the number of measures consumed, gives the amount of iodine per cent. in the sample.

This process is obviously incompatible with proto-compounds of iron, arsenious acid, and substances having similar chemical relations; but their presence would be immediately disclosed and their influence easily prevented.

Kelp and Kelp-liquor.

The direct application of the present process to kelp and kelp-liquors is evidently inadmissible, in consequence of the sulphides, sulphites, hyposulphites and sulphocyanides, which they invariably contain. All these ingredients act readily upon bichromate of potash, in presence of hydrochloric acid. They may however be effectually removed by cautiously treating the solution from the kelp with hydrochloric acid, and evaporating to dryness, repeating the operations if necessary, or till the above ingredients are decomposed. In the case of kelp, the following is an outline of the mode of procedure:—A known weight is exhausted with water in the usual manner, and the several liquors being mixed, are concentrated by evaporation, and set aside to crystallize. The mother-liquor is decanted and slightly supersaturated with hydrochloric acid, boiled and filtered. The filtrate is then evaporated completely to dryness, a little carbonate of soda being added towards the conclusion, if it be found that the hydrochloric acid is in such excess as to affect the iodide. This will be indicated by the liberation of iodine, and by the solution acquiring a dark colour. The dry residue is digested in a small quantity of cold water and filtered. The solution is then tested for the presence of the substances before named, when, if pure, it is transferred (wholly or in part, according to the quantity of kelp operated upon) to the alkalimeter, and subsequently dropped into the prepared solution of bichromate of potash and hydrochloric acid, as previously described. If however it should still contain any sulphite, hyposulphite, &c., the treatment with hydrochloric acid is repeated. It has been found that the extraction of the iodide from the residue by means of alcohol answers very well when the removal of the incompatible matters is attended with difficulty. The quantity of iodine in kelp is proportionately small, and of course subject

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to extensive variation. The amount extracted on the large scale from "drift-weed kelp" varies from 5 to 12 lbs. per ton, though larger quantities are said to have been obtained. From cut-weed kelp not more than 2 to 3 lbs. per ton have been extracted; and it is easy to conceive that the produce will be variable when these two kinds of kelp are mixed together. Not less therefore than 2 lbs. of drift-weed kelp should be operated upon, and in the case of cut-weed kelp, it will be advisable to use only 5 grs. of bichromate of potash in place of 10 grs.

The method of testing kelp-liquors is evident from the above outline of the mode of operating upon kelp itself.—*Communicated by the Author.*

Notice on a disputed Question connected with the Œconomy of the Steam-Engine. *By* JAMES APJOHN, M.D., Professor of Chemistry and Mineralogy, T.C.D., M.R.I.A.*

It has been frequently proposed to substitute the vapour of some volatile liquid, such as alcohol or æther, for that of water in the steam-engine, under the idea that by so doing fuel would be œconomized; and the proposal appears *primâ facie* plausible, seeing that their boiling-points are not only lower than that of water, but that the same is true of their specific heats, and of the latent heats of their vapours. This idea would seem to have struck at different times the minds of different persons, and the Rev. Mr. Cartwright, a gentleman of great mechanical genius, and celebrated for his mechanical inventions, actually devised a most ingenious form of steam-engine (see Phil. Mag., vol. i. 1st ser.), in which the piston was to be moved by the vapour of alcohol. Mr. Ainger, in a notice brought by him before the Royal Institution, London, in February 1830, on the œconomy of the steam-engine, would seem to be the first person who publicly dissented from such views; and he has certainly the merit of having shown the insufficiency of the data generally used by those who, previous to his time, calculated that the substitution of more volatile liquids for water would lead to a considerable saving of fuel. The conclusion however at which he arrives, that, leaving the original cost of the liquids out of consideration, water would be as œconomical a liquid as alcohol or æther, I believe to be quite erroneous; and as the question at issue is one of some practical

* A very brief and imperfect notice of this paper appeared in our last Number, taken from the 'Northern Whig.' By the kindness of the author, we are now enabled to give the entire paper.

We also take this opportunity of correcting a mistake into which we fell in noticing Dr. Apjohn's communication on a substance resembling *Pigotite* (not *Pigolite*). In the abstract, the author is represented to have stated that the substance was apparently identical with Pigotite. This is not the case; the analytical results obtained by Dr. Apjohn were quite irreconcilable with those arrived at by Prof. Johnston in his experiments on Pigotite, as will be seen by the following formulæ, the first of which is that given by Dr. Johnston, while the second represents the substance examined by Dr. Apjohn:—

1. $4Al^2O^3, C^{12}H^5O^8 + 27HO.$
2. $2Al^2O^3, C^{10}H^{10}O^{11} + 16HO.$—ED.

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importance, I shall proceed to state succinctly the method of calculation which I have employed in discussing it, and the precise results at which I have arrived.

As the vapours of different liquids have at their respective boiling-points the same elastic force, equal volumes of them will produce equal mechanical effects. In order therefore to the solution of the question under consideration, it will only be necessary to calculate the weights of the different liquids, water included, which give equal volumes of vapours, and to determine the quantities of caloric necessary for the conversion of these into vapour.

Now as the volume of a vapour, like that of any other form of matter, is represented by its weight or mass divided by its specific gravity, if we put

$$\frac{x}{s^1} = \frac{1}{s},$$

x being the weight of any vapour whose specific gravity is s^1, and s the specific gravity of the vapour of water, we shall get

$$x = \frac{s^1}{s},$$

that is, the weight of any liquid which at its boiling-point gives a volume of vapour equal to that given by a weight of water represented by unity at *its* boiling-point, is got by dividing the specific gravity of the vapour by that of steam.

But the specific gravities to be used in this computation are not those usually given in books, each of which is referred to a different unit, viz. air at the same temperature, and under the same pressure as the vapour; but the specific gravities of the vapours at the respective boiling-points of the several liquids, compared to the standard unit, viz. air at 60°, and under a pressure of 30. In the following table, the former specific gravities are found in the second, and the others in the third column, the latter being in each case got by multiplying the former by $\frac{518}{458+t}$, t being the boiling-point of the liquid which yields the vapour. In column 4 we have the weights which would give equal volumes of vapours, calculated by the expression $x = \frac{s^1}{s}$ already given, the values of s and s^1 being taken from column 3:—

1.	2. Spec. grav. referred to air at boiling-points.	3. Spec. grav. at boiling-points referred to air at 60°.	4. Weights giving equal volumes.
Water.....	0·622	0·480	1·000
Wood-spirit	1·120	0·950	1·979
Alcohol	1·613	1·322	2·754
Æther	2·586	2·397	4·993

It is now easy to assign the quantities of caloric necessary to produce an equal volume of the vapour of each liquid at their respective

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boiling-points, for these will obviously be represented by the expression

$$mc\{(t-50)+l\},$$

m being for each liquid its number in column 4, c its specific heat, t its boiling-point, and l the latent heat of its vapour at the temperature of ebullition. When, with the aid of the annexed table—

	Boiling-points.	Specific heats.	Latent heats.
Water	212°·0	1°·00	961°·8
Wood-spirit	151·7	0·67	475·2
Alcohol	172·4	0·64	374·4
Æther	100·4	0·50	163·8

which exhibits the specific and latent heats on which most reliance can be placed, the numerical calculation is made, the following are the results:—

Water	1129·0	1·000
Wood-spirit	764·8	0·676
Alcohol	875·5	0·775
Æther	534·7	0·473

The mere inspection of these numbers is sufficient to show that Mr. Ainger is in error, or that by substituting for water, wood-spirit, alcohol or æther, the same moving force will be obtained, and with a great saving of fuel. With wood-spirit about two-thirds, with alcohol about three-fourths, and with æther somewhat less than half the caloric required by water will suffice.

To the use, however, of such liquids there are obvious objections. Their cost is considerable compared to that of water; and as they evolve at atmospheric temperatures vapours of a considerable elastic force, they will, from imperfect condensation, resist the descent of the piston, and thus give rise to an appreciable loss of power. But notwithstanding this practical difficulty, which by the way is not, in the cases of alcohol and wood-spirit, one of a very formidable nature, the theoretic conclusion is no less certain, that equal volumes of the vapours of different liquids, formed at their respective boiling-points under the pressure of a single atmosphere, *do not* require for their production equal quantities of caloric.—*Communicated by the Author.*

On the Composition of Food in relation to Respiration and the Feeding of Animals. *By* J. B. Lawes, Esq. *and* Dr. J. H. Gilbert.

The general connexion of the *non*-nitrogenous constituents of food with respiration and the formation of fat in the animal body, on the one hand, and on the other that of the nitrogenous constituents with the formation in the body of compounds containing nitrogen, and with the exercise of force, are now fully admitted. But within and around these two main points there are still many open questions. It was usually maintained, and more especially when laying down rules in regard to the dieting of fattening animals, that the comparative value of food, *as such*, is to be measured by its per-centage of nitrogenous compounds. Bearing upon this point, the authors

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exhibited numerous tables of the results of a very extensive series of experiments upon the fattening of sheep and pigs. The several foods employed contained different proportions respectively of the *nitrogenous* and *non*-nitrogenous constituents; and the general arrangement was such, that each set of the animals to be compared had a fixed and limited quantity of one description of food, and was allowed to take *ad libitum* of another or complementary food; and thus, according to the composition of the respective foods, the animals were enabled to fix for themselves, in obedience to the demands of the system, the quantities of each class of constituents which it required. The result was, that when due allowance was made for the different respiratory and fat-forming *capacities* of the several digestible or assimilable *non*-nitrogenous constituents of the foods, and also for those which would probably become at once effete, the amounts consumed by a given weight of animal, of the same description, within a given time, and under otherwise equal circumstances, represented, in the different sets, with different descriptions of food, almost identical respiratory and fat-forming capacities; whilst, on the other hand, the quantities of the nitrogenous constituents taken into the system under the same circumstances varied, in the different cases, as much as from one to two or three. *Consumption* then was regulated by the respiratory and fat-forming exigences of the animal, rather than by the amount of nitrogenous constituents which the food supplied. This view indeed was only that to which we should naturally be led in applying the facts and principles generally admitted, when the rationale of the respiratory process, as such, was under consideration. But in the current methods of representing the equivalents of different foods, there would seem to be some inconsistency with those facts and principles.

From the same experiments it also appeared, that the amount of *increase in weight* of the fatting animals also bore a much closer relationship to the amount of the assimilable *non*-nitrogenous constituents of the food than to that of the nitrogenous ones. A certain liberal amount of nitrogen was indeed very important; but beyond a limit frequently exceeded in practice, the effect of an increased per-centage of nitrogen in the food, upon the *increase in weight* of the animal, was in a rapidly decreasing ratio. The authors considered therefore that the rule generally laid down, namely, that the comparative values of foods, *as such*, were measurable by the amounts of the nitrogenous compounds which they contained, required considerable modification. Of course, when the value of the *manure* was a matter of consideration, a new element was brought into the question.

Experiments, in which pigs were the subjects, were next adduced, showing that the *increase in weight* of the fattening animal contained much less nitrogen and a larger proportion of fat than was usually supposed; and it was stated, that experiments upon other animals, which would be published at some future time, also gave results in the same direction. It was also shown, by reference to direct experiment with pigs, in regard to the much-debated question, namely, whether fat was *formed* in the animal body from vegetable substances

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not containing it, or whether it was only *assimilated* from the food—that, in the instance cited, about *four times* as much fat had been stored up in the animal as it had taken of fatty substance in its food. This result was consistent in kind with that of the more recent investigations of MM. Boussingault and Persoz, which, though they had been somewhat called in question, the authors considered sufficiently conclusive. The formation of fat, even to a considerable and practically important extent, from the starch series of compounds, was demonstrated by the experiments now brought forward. MM. Dumas and Boussingault had, indeed, at one time, held this to be improbable; and other writers have done so more recently; but it would seem that the theoretical opinions of Professor Liebig on this point may be considered to be fully borne out.

Thus far the authors had only alluded to the feeding of fattening animals; but having calculated many human dietaries, and also from the consideration of the management of the animal body undergoing somewhat excessive labour, as for instance the hunting-horse, the racer, the cab-horse, and the fox-hound, and also pugilists and runners, they considered that the exigences of the respiratory system, in the cases at least of ordinary exercise of force, keep pace more nearly with the demand for nitrogenous constituents of food than is usually supposed. A consideration, indeed, of the habits of those of the labouring classes who are under- rather than over-fed, would show that they *first* have recourse to fat meat, such as pork, rather than to those which are leaner and more nitrogenous; thus indicating that the first instinctive call is for an increase of the respiratory constituents of food. It cannot be doubted, however, that the higher classes do consume a larger proportion of nitrogenous food in the form of meat, though it is probable that with it more fat (which is one of the highest of the respiratory constituents of food) is taken into the system than is generally imagined. Fat and butter, indeed, may be said to have about twice and a half the capacity in this respect of starch, sugar, &c. It should be remembered, too, that the classes which consume most meat are also those which consume most butter, sugar, and in many cases alcoholic drinks also. It is further worthy of remark, that where labour is expended in the manufacture of staple articles of food, it has generally for its object the concentration of the *non*-nitrogenous or respiratory constituents. Sugar, butter, and alcoholic drinks are notable instances of this. Cheese, which at first sight might appear an exception, is in reality not so; for those cheeses which bring the highest price are always those which contain the most butter; whilst butter itself is always dearer than cheese.

In conclusion, the authors are not to be understood as in any way depreciating the value of a somewhat liberal amount of nitrogen in food; but they consider that, on the current views, too high a relative importance is attributed to it; and that it would conduce to further progress in this most important field of inquiry, if the current opinions on the subject were somewhat modified.—*Abstract communicated by the Author.*

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Cocinone, Myristone and Laurostearone.

By W. DELFFS *and* A. OVERBECK.

Among the homologous series of organic compounds, that of the fatty acids occupies the first place, insofar as it comprises the greatest number of members. For this reason they and their derivatives furnish the best demonstration of the law, that homologous compounds differ from each other in composition by $n\ C^2\ H^2$. However, a very erroneous opinion might be formed as to the accuracy of the principle, that the characters of the members of a series are determined by their position in it, if the data found in chemical works are admitted to be correct. This is sufficiently shown by the following table, in which the observed boiling-points of the *acetones*, $= C^{2n}\ H^{2n}\ O^2$, are placed by the side of those probable according to theory:—

		Boiling-point. Calculated.	Observed.	
Acetone ..	$C^6\ H^6\ O^2$	132·8	132·8	Kopp*.
Propione ..	$C^{10}\ H^{10}\ O^2$	212·0	212·0	Morley†.
Butyrone ..	$C^{14}\ H^{14}\ O^2$	291·2	291·2	Chancel‡.
Valerone ..	$C^{18}\ H^{18}\ O^2$	370·4	212·0 − x	Löwig§.
Caprone ..	$C^{22}\ H^{22}\ O^2$	449·6	329·0	Brazier and Gosleth‖.
Aboleone ..	$C^{26}\ H^{26}\ O^2$	528·8	?	
Caprylone..	$C^{30}\ H^{30}\ O^2$	608·0	352·4	Guckelberger¶.

The boiling-points of the first three bodies show a regular progression, the constant difference of which is 79°·2, and the boiling-points of the others are calculated upon the assumption that the same relation holds good for them. The difference between the calculated and observed data for the last three bodies is so great, that either the theory must be ill-founded or the data given incorrect.

Similar discrepancies occur with regard to the melting-points of the higher members of this series. Bussy states that stearone melts at 166°·6, and margarone at 170°·6, and St. Evre** describes cocinone as being liquid at the ordinary temperature. The melting-

* Pogg. Ann., lxxii. 236. † Ann. der Chem. und Pharm., lxxviii. 187.

‡ *Ibid.*, lii. 295.

§ Pogg. Ann., xlii. 412. Löwig states that valerone boils in a water-bath far below 212°. ‖ Ann. der Chem. und Pharm., lxxv. 256. ¶ *Ibid.*, lxix. 250.

** Ann. de Chim. et de Phys., iii. ser. xx. 29.

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points of the former two would therefore be higher than those of the corresponding acids, and that of cocinone lower, for stearic acid melts at 158°, margaric acid at 140°, and cocinic acid at 95°.

These facts are sufficient grounds for instituting a new examination of those acetones with regard to which there are discrepancies between theory and observation.

These bodies were prepared by submitting the neutral lime, or baryta salts of the fatty acids (obtained by precipitating an alkaline soap with chloride of calcium or barium), to dry distillation: the decomposition is then—

$$\underbrace{2CaO + C^{22} H^{21} O^3}_{\text{Cocinate of lime.}} = 2(CaO + CO^2); \underbrace{C^{42} H^{42} O^2}_{\text{Cocinone.}}.$$

If prepared according to the ordinary mode, by distilling the acids with an excess of alkaline earth, there is danger of the acetone being mixed with the corresponding hydrocarbon, for—

$$C^{22} H^{21} O^3 + HO; \; 2CaO = 2(CaO\,CO^2); \; C^{20} H^{22};$$

and any such admixture would account for the above discrepancies in the boiling- and melting-points, if, on the other hand, it could be imagined that the analyses would on this assumption agree with the calculated formulæ.

Even when the acetones are prepared from neutral salts, secondary products are formed, which mix with them, and can only be separated by frequent crystallization from boiling absolute alcohol; consequently it is not worth while to employ perfectly pure acids. In recrystallizing the raw product of the distillation, nearly absolute alcohol must be used, as the acetones are less soluble the higher their equivalent.

The analysis of cocinone with chromate of lead gave—

				Found.	
			Calculated.	I.	II.
Carbon.....	42	252	81·29	..	81·29
Hydrogen	42	42	13·55	13·76	13·86
Oxygen	2	16	5·16		

Cocinone crystallizes from boiling absolute alcohol in light, brilliant, white flakes. It has neither smell nor taste. It dissolves in æther more easily than in alcohol. The boiling-point is too high to be determined by the mercury-thermometer.

Myristone.—Pure myristone was obtained by repeatedly treating commercial Muskat butter with æther, crystallizing, and finally exposing for a long time to the heat of a water-bath to remove any remaining traces of volatile oil. A mixture of equal parts of æther and alcohol of 0·811 spec. grav. was found best adapted for the last crystallization. The myristone thus obtained was saponified with soda, the hot solution precipitated with chloride of calcium, the myristate of lime dried and distilled in small portions, the temperature being regularly and gradually raised. Myristone then distilled over in colourless drops, which solidified in the neck of the retort. The

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operation was stopped as soon as brown secondary products began to appear, as they render the purification extremely difficult.

By repeated crystallization from absolute alcohol and treatment with animal charcoal, the myristone was obtained in the form of brilliant white flakes, having a pearly lustre, and destitute of taste or smell. It solidifies after melting to a radiated crystalline mass, and becomes strongly electric when rubbed. It crystallizes from æther with a remarkable molecular agitation.

The analysis, by means of chromate of lead, of myristone, which had been kept for a long time in a state of fusion in a water-bath, gave—

Carbon	81·81	81·81	25 =	81·96
Hydrogen	14·07	13·95	25	13·65
Oxygen	4·12	4·24	1	4·39

Laurostearone.—The preparation and purification were conducted in the same way as those of myristone. When pure, it crystallizes from absolute alcohol in brilliant white flakes, but with a less pearly lustre than that body. It solidifies after melting to a radiated crystalline mass, and becomes very strongly electric when rubbed.

The analysis of thoroughly dried laurostearone gave—

Carbon	81·42	81·04	23 =	81·65
Hydrogen	13·82	14·10	23	13·61
Oxygen	4·76	4·86	1	4·74

The results of the analyses are, from their conformity with the calculated compositions, a contribution, though slight, to the completion of the homologues of the fatty acids and their derivatives, and give especial interest, inasmuch as they sufficiently point to a general law to instigate chemists to carry out the development of these series; and it appears not to be venturing too much to assume that the theory of homologues will perhaps in a short time occupy, in a theoretical point of view, a prominent position with regard to the study of organic bodies.

The determination of the melting-points was conducted as follows:—The melted substances were drawn up into a thin open tube, slightly contracted at one end, about an inch and a half long and a line in external diameter, so that it was about two-thirds filled with the solid substance. The tube was then suspended, together with a thermometer, in a beaker glass containing water, so that the upper part of the tube was a little above the water; heat was then gradually applied, and the temperature observed at the moment when the melted substances rose from the pressure of the water. This method obviates all irregularity in the melting-points, which were found to be—

Cocinone	$=C^{42}H^{42}O^{2}$	136°·4 F.
Laurostearone	$=C^{46}H^{46}O^{2}$	150°·8
Myristone	$=C^{50}H^{50}O^{2}$	167°·0

These melting-points show a regular increase of from 14°·4 to 16°·2. If this increase obtains throughout the following parts of the series, stearone, $C^{66}H^{66}O^{2}$, would melt at 228°·2, while Bussy gives

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166°·8, and Redtenbacher 179°·6 as the melting-point. Bussy's statement, 86°, would nearly correspond with theory if it referred to the scale of Reaumur. Dr. Flückiger is at the present moment engaged in the preparation of stenzone and the determination of its melting-point.—Poggendorff's *Annalen*, lxxxvi. 527.

On Stibmethylium and its Compounds. By H. S. Lanbolt.

[Continued from p. 385.]

Monosulphuret of Stibmethylium, $StMe^4S$.—The compound is most readily obtained in the following manner:—An alcoholic or watery solution of oxide of stibmethylium is divided into two equal parts, one of which is to be perfectly saturated with sulphuretted hydrogen gas, and the other afterwards added to it. If the fluid be now rapidly evaporated without the contact of the air, which is best performed in a retort, the compound remains in the form of an amorphous green powder. It possesses a strong smell like mercaptan, and is readily taken up by water and alcohol. In æther it is insoluble. Its solutions are colourless, and give a black precipitate with nitrate of silver. It appears to be rather volatile, for if a watery or alcoholic solution of it be distilled, the distillate contains a not inconsiderable quantity of sulphuret of stibmethylium. When heated in a tube, it is first melted, and afterwards becomes decomposed with evolution of vapours, which take fire spontaneously; there remains a hard yellowish sublimate of sulphuret of antimony.

If the sulphuret of stibmethylium be brought into contact with the air, it becomes very rapidly oxidized, and changes into a yellow powder, which gradually becomes white; this is perfectly soluble in alcohol, but is no longer so in water. The solution gives with nitrate of silver a precipitate, which is at first brown, but soon becomes black. When æther is poured over it, it becomes changed into a soft greasy mass, but does not dissolve. If this white product of oxidation be heated on platina foil, it acquires at first a fine dark green colour, which disappears on cooling; if the heat be further increased, it becomes white again, and then takes fire.

The sulphur can only be approximately determined in consequence of the readiness with which the substance becomes oxidized. A certain quantity of sulphuret of stibmethylium, weighed in a close vessel, was quickly dissolved in water in a flask, and a solution of acetate of lead immediately added to it. A yellowish-red flocculent precipitate was formed, which disappeared after a short time, whilst black sulphuret of lead separated. This was collected on a filter, completely oxidized with nitric acid, and the solution of nitrate of lead evaporated with an excess of sulphuric acid, and heated to redness.

Carbon		8 =	48	23·41
Hydrogen		12	12	5·85
Antimony		1	129	62·93
Sulphur	8·86	1	16	7·81

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From the circumstance that a solution of oxide of stibmethylium boiled with sulphur furnishes milk of sulphur on the admixture of an acid, we may conclude that still higher compounds of sulphur with stibmethylium might be obtained.

Iodide of Stibmethylium, StMe⁴ I.—The mode of preparing this compound has already been given. The iodide of stibmethylium crystallizes in forms belonging to the hexagonal system; it forms remarkably beautiful, six-sided tablets, the lateral faces of which all intersect at 120°, whilst the terminal three faces are plane. The diameter of the tablets is as much as from 10 to 15 millims. The crystals are usually scaliform; they contain water mechanically enclosed, and consequently decrepitate on the application of heat.

This salt is very readily soluble in water and alcohol. 1 part of iodide of stibmethylium is dissolved by 3·3 parts of water at 73° F. In æther it is soluble with difficulty. Its taste is saline, leaving a bitterness in the mouth. If the compound be heated in a tube closed at one end, it first falls to powder, and begins to be decomposed at 392° F., at which temperature it gradually disappears entirely. During this, thick white fumes are evolved, possessing the odour of stibmethyle, which in part become deposited as a coating on the inside of the tube, but which principally reach the mouth and take fire there, forming always rings of smoke similar to those formed by phosphuretted hydrogen gas. Of the coating deposited on the tube, only a small portion is dissolved off by boiling with water; if nitrate of silver be added to this fluid, a precipitate is formed consisting of iodide of silver and metallic silver. The reduction of the nitrate of silver is no doubt effected by pure stibmethyle or stibmethylium, which must have been set free during the decomposition. As however iodide of silver is also thrown down, a small portion of iodide of stibmethylium appears to be sublimed unchanged.

The iodide of stibmethylium agrees perfectly in its other properties with iodide of potassium. Muriatic acid decomposes it with formation of chloride of stibmethylium; chlorine, bromine, and nitric acid separate iodine instantaneously. If concentrated sulphuric acid be poured over it, fumes of hydriodic acid are evolved, just as with iodide of potassium, whilst iodine is set free, with formation of sulphurous acid. The watery solution of iodide of stibmethylium has the property of dissolving no inconsiderable quantity of the yellow modification of the iodide of mercury; if red iodide of mercury be employed and boiled, it changes into the yellow modification, and only then becomes dissolved. If the fluid be allowed to cool, a considerable quantity of the iodide of mercury is again separated, and always in the yellow modification.

The iodide of stibmethylium exhibits a very remarkable behaviour towards the electric current. If a watery solution of it be subjected to electrolysis, iodine, together with a small quantity of oxygen gas, is separated at the negative pole, an active evolution of gas takes place at the positive pole, whilst at the same time the fluid becomes milky, acquires an alkaline reaction, and begins to emit the odour of stibmethyle. The gas evolved at the positive pole, the volume of

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which is about ten times that of the oxygen separated at the other, contains antimony, possesses the odour of stibmethyle in a remarkable degree, and readily takes fire, with the production of a white smoke. If this be shaken with an alcoholic solution of iodine, its colour disappears, and the volume of the gas is diminished. This deportment leads to the supposition that the gaseous body may be pure stibmethylium, although its physical properties are different from those of the compound obtained by the distillation of iodide of stibmethylium with antimoniuret of potassium. Its further examination was unfortunately obliged to be postponed in consequence of want of material. As oxygen gas appeared at one pole, decomposition of water also took place.

If iodide of stibmethylium be added to strong starch paste, and the mixture spread upon filtering-paper, such paper behaves towards ozone in exactly the same manner as that prepared with iodide of potassium; it appears even to be still more sensitive. If an aqueous solution of iodide of stibmethylium be poured over amalgam of sodium, successive little explosions take place, which are accompanied by an appearance of fire; metallic antimony is separated.

It has already been stated, in the general review of the compounds of stibmethylium, that iodide of stibmethylium gradually becomes decomposed by repeated evaporation, whilst a small quantity of a yellow substance, insoluble in water, is formed, which however could not be further investigated. The odour of stibmethyle was always evolved at the same time. This yellow substance also appears, although not constantly, when solid iodide of stibmethylium is exposed to the light of the sun.

The combustion of this compound is readily effected with oxide of copper. Copper shavings are placed in the anterior portion of the combustion-tube to retain the iodine. The determination of the iodine of the salt, previously dried under the desiccator, was performed in the usual manner by means of nitrate of silver. By this means we always find 1 per cent. more iodine than is required by the formula, which may here arise from the circumstance (although indeed too much iodine is generally found in such cases) that fresh iodide of stibmethylium could not be employed in this determination:—

Carbon	15·23	15·48	15·79	15·65	8 = 48	15·17
Hydrogen	4·19	4·03	4·10	..	12	12	3·79
Antimony	39·74	39·31	38·85	..	1	129	40·86
Iodine	40·84	41·18	41·26	41·36	1	127	40·18

Bromide of Stibmethylium, $StMe^4Br$.—This compound is most readily procured by the decomposition of iodide of stibmethylium with bromide of mercury. If the fluid be filtered from the iodide of mercury and evaporated, a beautiful salt, soluble in alcohol and water, but insoluble in æther, is obtained; its form could not be exactly determined. Its taste is saline and bitter. When heated, it evolves white vapours, which take fire in the air; a separation of bromine by this means was not observed. On pouring concentrated

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sulphuric acid over it, fumes of hydrobromic acid immediately result; nitric acid separates bromine. Towards metallic salts a solution of bromide of stibmethylium behaves exactly like bromide of potassium. Bromide of stibmethylium was analysed in the same manner as the iodide:—

Carbon	18·38	8 =	48	17·84
Hydrogen	5·05	12	12	4·46
Antimony	47·07	1	129	47·96
Bromine	29·49	1	80	29·74

Chloride of Stibmethylium, $StMe^4Cl$.—This compound is best procured by adding to a watery solution of iodide of stibmethylium a hot solution of chloride of mercury, just so long as a precipitate of iodide of mercury is produced. If the fluid be filtered off, and evaporated on the water-bath to crystallization, chloride of stibmethylium separates in white crystals, belonging to the hexagonal system; six-sided tablets, such as occur in iodide of stibmethylium, could be distinctly observed. The crystals are very readily soluble in water and alcohol, nearly insoluble in æther. Their taste is bitter and saline. If the salt be heated in a tube, it puffs up; and when more strongly heated, disappears gradually, with evolution of fumes, which take fire spontaneously on coming in contact with the air. The white sublimate, which is deposited on the cooler parts of the tube, contains chloride of antimony.

It is worthy of remark, that when a hot solution of chloride of mercury is poured into a cold solution of iodide of stibmethylium, a voluminous yellow iodide of mercury is often obtained, which can only be transformed with great difficulty into the red modification. Trituration, heat, &c. have scarcely any influence upon it. But if, on the other hand, one of the two solutions, or both, be employed cold or warm, and the solution of chloride of mercury be poured into that of iodide of stibmethylium, or the reverse (except in the case above described), the iodide of mercury is obtained in the yellow form, but always changes spontaneously into the red with more or less rapidity.

Chloride of stibmethylium does not appear, like muriate of ammonia, to form double compounds with the salts of magnesia; for if chloride of stibmethylium be added to a solution of a magnesian salt, and a solution of oxide of stibmethylium or ammonia be poured into it, a precipitate of hydrate of magnesia is the result. Concentrated sulphuric acid immediately evolves muriatic acid gas from chloride of stibmethylium. Analysis gave:—

Carbon	..	..	8 =	48·0	21·38
Hydrogen	..	..	12	12·0	5·35
Antimony	..	..	1	129·0	57·46
Chlorine	15·60	15·70	1	35·5	15·81

Chloride of Platinum and Stibmethylium, $StMe^4Cl, PtCl^2$.—If chloride of platinum be added to a watery solution of chloride of stibmethylium, a yellow crystalline precipitate is formed, which may

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be dissolved by the addition of water and boiling. On cooling, small crystals of the double salt separate, which are dried between paper.

The double chloride of platinum and stibmethylium is a beautiful orange-yellow crystalline powder. It is the most difficult of solution of all the compounds of stibmethylium yet known, and in respect of its solubility in water stands between potassio-chloride of platinum and sodio-chloride of platinum. When much water is poured over it, it communicates a yellow colour, but only dissolves completely when boiled. In alcohol and æther it is completely insoluble, very difficult of solution in alkalies, but more easy in muriatic acid. If the double salt be heated, it acquires a black colour, and very soon takes fire; there remains an alloy of platinum and antimony fused into globules, from which the latter metal can only be imperfectly removed by boiling in nitromuriatic acid.

It was attempted to determine the amount of platinum contained in it in the following manner:—1 part of the compound was intimately mixed with 2 parts of powdered nitrate of potash, ½ part of hydrate of potash then added, and the whole kept in a fluid state in a porcelain crucible for half an hour. The mass was then treated with water, the separated rust-coloured compound of potash with oxide of platinum collected on a filter, dried, and exposed to heat. The residue was boiled with muriatic or nitric acid, and the metallic platinum obtained washed upon a filter, dried and exposed to a red heat. The platinate of potash must not be treated with muriatic acid whilst moist, as it dissolves slowly in it, and the decomposition by sulphuric acid is also not complete in the cold:—

Carbon	..	..	8 =	48·0	12·18
Hydrogen	..	..	12	12·0	3·04
Antimony	..	..	1	129·0	32·72
Platinum	24·75	25·62	1	98·7	25·02
Chlorine	..	..	3	106·5	27·02

Cyanide of Stibmethylium.—If to a solution of iodide of stibmethylium a solution of cyanide of mercury be added, a yellowish precipitate is produced at first, apparently consisting of iodide of mercury, which soon becomes redissolved without the application of heat. A slight odour of hydrocyanic acid is evolved, especially when the mixture is warmed. By evaporation, hard shining crystals are obtained, which doubtless consist of iodide of mercury and cyanide of stibmethylium, corresponding with the compound of iodide of mercury and cyanide of potassium. The investigation of this compound could not be carried further from the want of material.

Neutral Sulphate of the Oxide of Stibmethylium.—This salt is best obtained by adding to a watery solution of iodide of stibmethylium a hot solution of sulphate of silver as long as a precipitate of iodide of silver is produced. By filtering and evaporating the fluid on the water-bath to crystallization, colourless crystals are obtained, which may be pressed between paper and dried in the air. Their form appeared to be rhombic.

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These crystals contain water. They agree with the formula $(StMe^4)O,SO^3+5Aq$. They do not deliquesce in the air, but when placed under the desiccator they lose a part of their water, and fall to a white powder; the last trace of water however only escapes at 212° F. If the salt be more strongly heated in a chloride of zinc bath, it begins to decompose slowly at 248° to 266° F., emitting an odour of stibmethyle; it melts at 302° F.; at a still higher temperature, 356° F., complete decomposition, with appearance of fire, takes place. By long exposure to a temperature of 212°, gradual decomposition appears to take place.

The sulphate of the oxide of stibmethylium is very readily soluble in water; if water be poured upon the anhydrous salt, it becomes strongly heated. It is also soluble in alcohol, but insoluble in æther. Its taste is saline and bitter.

For the determination of the sulphuric acid, the salt was dissolved in water, and chloride of barium added to the solution. In No. I. the anhydrous salt was employed, in No. II. the crystals containing water, and the sulphuric acid calculated from the anhydrous compound. The analyses gave 15·60 and 15·24 water. The anhydrous sulphate of the oxide of stibmethylium then furnished—

Carbon.....	..	..	8 =	48	20·25
Hydrogen	..	..	12	12	5·06
Antimony.....	..	..	1	129	54·43
Oxygen	..	..	1	8	3·38
Sulphuric acid....	17·09	16·78	1	40	16·88

It was also attempted to form an alum by mixing 1 atom of sulphate of the oxide of stibmethylium with 1 atom of sulphate of alumina, but without success. The two salts crystallized out together unchanged.

Bisulphate of the Oxide of Stibmethylium, $StMe^4O,HO+2SO^3$.—To prepare this salt, exactly 1 atom of hydrate of sulphuric acid is added to a watery solution of 1 atom of the neutral sulphate; by numerous recrystallizations, beautiful, hard, transparent crystals are obtained, amongst which four-sided tablets with obliquely-truncated edges occur. The salt is very readily soluble in water, less easily in alcohol, and nearly insoluble in æther. It possesses a strongly acid taste, and leaves a bitter taste in the mouth. On being heated, it behaves exactly like the neutral sulphate. If the salt be dissolved in a small quantity of water, alcohol added to it and again thrown down by æther, and this operation be several times repeated, the neutral sulphate of the oxide of stibmethylium is at last obtained. In this respect it behaves exactly like the bisulphate of potash.

This salt contains no water of crystallization. The basic water, like that of the bisulphate of potash, cannot be driven off by exposure to a heat of 248° F.:—

Carbon.....	16·98	..	8 =	48	16·78
Hydrogen	4·43	..	13	13	4·55
Antimony	..	..	1	129	45·11
Oxygen	..	..	2	16	5·59
Sulphuric acid....	28·01	28·15	2	80	27·97

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Nitrate of the Oxide of Stibmethylium, $StMe^4O, NO^5$.—Nitrate of silver is added to a watery solution of iodide of stibmethylium until a precipitate is no longer formed; the fluid is then filtered off and evaporated to crystallization.

The crystals are anhydrous. Their form could not be exactly determined; but if a drop of the watery solution of the salt be allowed to evaporate on a glass plate under the microscope, exactly the same coarsely-radiated forms as in nitrate of potash may be observed.

The nitrate of the oxide of stibmethylium is readily soluble in water, but with difficulty in alcohol and æther. It has a bitter and harsh taste; it cannot be called cooling. When heated, it first expels white fumes, which immediately take fire; the entire mass then explodes with a large white flame, exactly like a mixture of nitrate of potash and carbon. This salt appears to be very constant, as it may be boiled with concentrated sulphuric acid without decomposition.

The determination of the nitric acid was effected in the following manner:—The compound was dissolved in water, an excess of baryta-water added to it, and the fluid evaporated to dryness on the water-bath. The residue was treated with alcohol, and carbonic acid gas passed through the fluid, in order to decompose any compound of barium with oxide of stibmethylium which might be soluble in the alcohol; nothing of this kind however appeared to be formed, as no carbonate of baryta was separated. The alcohol was poured off, the residue dissolved in water, the excess of baryta precipitated by carbonic acid, and the baryta then thrown down from the solution of nitrate of baryta filtered from the carbonate of baryta by means of sulphuric acid:—

Carbon	..	8 =	48	19·13
Hydrogen.....	..	12	12	4·78
Antimony.....	..	1	129	51·39
Oxygen.....	..	1	8	3·19
Sulphuric acid....	20·91	1	54	21·51

Carbonate of the Oxide of Stibmethylium.—The neutral carbonate is procured by the decomposition of a solution of iodide of stibmethylium by freshly-precipitated carbonate of silver. If the filtered fluid be evaporated on the water-bath, there remains an indistinctly-crystallized, somewhat yellowish, transparent mass, which very readily deliquesces in the air, possesses an alkaline reaction, and is readily soluble in water and alcohol, but in æther with great difficulty. Its taste is bitter and alkaline. The compound is very unstable, as it immediately begins to smell of stibmethyle. When heated, it acts like the other compounds of stibmethylium. It appears to contain no water of crystallization.

If carbonic acid gas be passed through a solution of the neutral carbonate or of oxide of stibmethylium, and the solution be afterwards evaporated, the bicarbonate is obtained. This salt crystallizes with difficulty in small needles arranged in stars,

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which deliquesce in the air; it is readily soluble in water and alcohol, but insoluble in æther. It has an alkaline reaction and a bitter taste. Kept in the solid form, it very soon becomes decomposed, like the neutral carbonate. The watery solution of this salt, when heated, evolves carbonic acid gas, and gives no precipitate with neutral salts of magnesia. These two compounds could not be analysed in consequence of their deliquescence and ready decomposition; they no doubt however agree with the formulæ $(StMe^4)O$, CO^2 and $(StMe^4)O, HO+2CO^2$.

Acetate of the Oxide of Stibmethylium is produced by the decomposition of the iodide by acetate of silver. This compound is still more unstable than the carbonate; if its watery solution be evaporated, a dark coloured mass, of a syrupy consistence, with the odour of stibmethyle, is obtained, which cannot be brought to crystallize perfectly.

Bitartrate of the Oxide of Stibmethylium is much more soluble in water than the bitartrate of potash.

Oxalate of the Oxide of Stibmethylium is obtained by neutralizing a solution of oxide of stibmethylium with oxalic acid. If the fluid be evaporated, the result is a distinctly crystallized stable salt, which is readily soluble in water, and with more difficulty in alcohol; it gradually deliquesces in the air, and contains a remarkable quantity of water of crystallization.—*Mittheil. d. Naturforsch. Gesellsch. in Zürich*, Nos. 72, 73 and 74.

ANALYTICAL CHEMISTRY.

On a new Reagent for Ammonia, and a Method for its Quantitative Estimation. *By* F. L. Sonnenschein.

It has already been shown*, that for the formation of the yellow precipitate in a liquid containing molybdic acid, three conditions are necessary, namely, the presence, besides molybdic acid, of ammonia and phosphoric acid in *definite* proportions. This circumstance, upon which depends the application of molybdate of ammonia, not only for the detection, but also for the quantitative determination of phosphoric acid, led to the idea that a solution containing two of the above-mentioned substances must be a reagent for the third; or, in other words, phosphoric acid and ammonia serve as a reagent for molybdic acid, phosphoric acid and molybdic acid as a reagent for ammonia, in the same way as molybdic acid and ammonia are a reagent for phosphoric acid. On taking into consideration the relative quantities of these substances necessary for the production of the yellow precipitate, it is evident that, as the quantity of molybdic acid must be 30 times as great as that of the phosphoric acid and 15 times as great as that of the oxide of ammonium, the method does not afford a good means of detecting or estimating molybdic acid, though, on the contrary, it admits of the detection

* Page 390 of the present volume.

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of ammonia with great delicacy, since the yellow precipitate in question contains only 0·747 per cent. of oxide of ammonium. Sonnenschein has investigated this subject for the purpose of deciding upon the accuracy of his conclusion.

On adding to a solution of molybdate of soda acidified with nitric or hydrochloric acid an adequate quantity of phosphoric acid ($MO^3 : PO^5 = 30 : 1$), no precipitate is formed, merely a yellow colour produced. The formation of the precipitate depends upon the presence of ammonia; consequently ammonia may be detected by such a liquid.

In preparing this solution for use as a test, it must be remembered, that when nitric acid is used for acidifying it, an acid salt may easily be formed, which by the inexperienced might be mistaken for the precipitate sought for, although it differs from this in having a brighter colour. It is therefore more convenient to employ hydrochloric acid, to heat the liquid, if any cloudiness appears to remove it by a further addition of acid, and then to add the proper quantity of phosphoric acid. The gold-coloured liquid thus obtained may be employed as a test for ammonia. However, as it is difficult exactly to hit upon the right proportions, it is better to adopt the following method in preparing the solution. The yellow precipitate produced in molybdate of ammonia by phosphoric acid is freed from ammonia by ignition, the dark-coloured residue oxidized by heating with nitric acid, the excess of which is driven off by heating, and the residue dissolved in the requisite quantity of carbonate of soda. If the solution has a bluish or greenish colour, the above process must be repeated.

The salt thus obtained is dissolved in water made strongly acid with hydrochloric acid and the liquid heated, any precipitate which may be formed being dissolved by more acid. By this means the substances are obtained in solution in the right proportions. In employing this liquid as a test, it must be remembered that the yellow precipitate has in general the characters of an insoluble salt, which forms soluble compounds only with alkalies and magnesia, and can only be dissolved by an excess of non-volatile organic acids; consequently influences of this kind must be avoided.

The sensibility of the reagent must be ascertained by means of a solution of chloride of ammonium of known strength. A solution containing only $\frac{1}{10,000}$th gave a distinct precipitate, and even one containing only $\frac{1}{80,000}$th, but not until the liquid had stood a long time. This extreme sensibility, which far exceeds that of chloride of platinum or tartaric acid, is not the only advantage which this method presents; the circumstance that the presence of free acids and other salts* is not of any consequence, also increases its applicability. For the same reasons, it is to be preferred to protonitrate of mercury, which only indicates the presence of free ammonia.

As the subject appeared to be of interest, Sonnenschein examined

* Potash salts alone form a similar precipitate, however only when the solution is tolerably concentrated.

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several substances for ammonia in this way. The following are the results he has obtained:—Fresh urine gives a flocculent greenish precipitate with the liquid, the supernatant liquid being coloured blue by reduced molybdic acid. The ammoniacal precipitate is not formed until after a long time, but then very distinctly.

Urine, when mixed while fresh with alcohol, gives a much smaller flocculent precipitate, the liquid is coloured greenish, and the ammoniacal precipitate is not formed even after it has stood a long time.

After eating asparagus, the urine gives *immediately* the ammoniacal precipitate. It follows from this that urine does not always contain ammoniacal salts, but that they are generally formed after a time, and that their formation is prevented by alcohol.

Urea behaves indifferently towards the solution.

The gradually progressive formation of ammonia in hydrocyanic acid may be distinctly recognised.

The presence of ammoniacal salts in the juice of beet-root was likewise detected in the most unmistakeable manner.

The flocculent precipitate which the reagent produces in solutions of organic substances is in many cases inconvenient, but they can be removed previously by precipitants which have no influence upon ammoniacal salts. When there is no phosphoric acid present, a solution of molybdate of soda made acid with hydrochloric acid may be conveniently used for this purpose.

In order to examine whether atmospheric air contained ammonia, several two-necked bottles were about a quarter filled with the phospho-molybdic acid*, and by means of a respirator the air drawn through in such a way that it must pass through the liquid. The ammoniacal precipitate was very soon formed; but as at the locality where the experiment was conducted there was an abnormal generation of ammonia, no general inference can be drawn from it. Sonnenschein however intends to repeat it under more favourable circumstances.

The question as to whether this method is applicable for the quantitative estimation of ammonia, requires for its solution in the first place, that it should be determined with certainty whether the composition of the precipitate is constant, and whether it can be completely separated from other substances. The former has been put beyond a doubt by numerous experiments, and the latter was tried in the following manner:—Known quantities of ammoniacal salts were mixed with the most different salts, with the exception of potash salts, and the solution precipitated with phospho-molybdic acid. They were allowed to stand for eight hours, the precipitates then collected upon weighed filters, washed with dilute hydrochloric acid, as pure water passed through milky, and dried at 212° F. The quantity of ammoniacal salt was then calculated from the weights of the precipitates, assuming that they all contained 6·747 per cent. of oxide of ammonium. The experiments furnished results which were tolerably accurate; however, it is requisite that they should be repeated in far greater number than has yet been possible, in order

* This name may be applied to the reagent.

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to be able to speak with certainty as to the applicability of the method to quantitative analysis.—*Journ. für Prakt. Chem.*, lvi. p. 302.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Process for imparting greater Liveliness to Indigo-blue in Stuffs. By L. Guillouet.

This discovery consists in exposing the stuffs coloured with indigo to the pressure of steam at an elevated temperature.

The blue colouring matter of the indigo is insoluble, and in order to fix it upon the stuffs, it is necessary to deoxidize it with green vitriol and lime. By dipping the stuffs into a solution of deoxidized indigo a darker or lighter colour is obtained according to the length of the immersion.

Indigo is also of a volatile nature, and this is in fact one of its characteristic properties. It occurred to me therefore to turn this property to account by exposing the stuffs coloured with indigo to the action of a high temperature, under constant pressure in air-tight metallic vessels, strong enough to resist an internal pressure sufficient to act upon the molecules of the indigo to incorporate them with the fibres of the stuff, and thus produce a change in the physical constitution of the indigo.

The form of the vessels employed is immaterial, but they must be furnished with a safety-valve and also with a cock, through which the atmospheric air may escape on the introduction of the steam.

The stuffs dyed with indigo are laid one upon another in the vessel in question upon a wooden pan, and enclosed in a cloth, which serves to prevent their coming in contact with the sides of the vessel, and also to absorb the moisture which is produced at the first introduction of the steam. The steam is then allowed to flow in at a pressure of from 2 to 6 atmospheres. After the lapse of about twenty minutes or half an hour, the cover of the apparatus is removed, and the stuffs taken out and left to cool, when they may be folded and packed.

This operation communicates a violet tinge to the colour of the indigo, without in the least injuring the other true colours fixed on the stuff, which, on the contrary, become fuller and brighter. The web loses considerably in length in the operation, but the loss of breadth is scarcely perceptible; at the same time a thicker and finer texture and more body and softness are obtained.—*Schweig. Gewerbeblatt*, xi. p. 98.

Improvement in the Production of the "Bleu de France" on Wool.

The method at present in use for the production of "bleu de France" on wool, consists in boiling the wool in a bath containing

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ferridcyanide of potassium, an acid and chloride of tin, until the pure blue colour is produced. In the course of this operation, much cyanogen escapes in the form of hydrocyanic acid. The loss of this substance, which is of so much importance in the formation of the blue colour, led to the idea of altering the process as far as possible in such a manner as to retain the whole or greater part of the cyanogen in the bath, and precipitate it in combination with iron upon the fibres of the wool. Experiments undertaken with this view showed that this end can be attained by adding to the bath a salt of oxide of iron; the best is perchloride of iron. The dyeing takes place in the following manner:—The ferridcyanide of potassium is first dissolved in the bath; a small portion of the acid to be used is then added, and afterwards the chloride of tin and chloride of iron. The bath is now clear, and of a brownish colour. The wool, well-washed and lukewarm, is then put in, and the whole heated to boiling. The wool immediately acquires a dark green colour, and by boiling, after the addition of the remainder of the acid, becomes of a fine blue colour.

The experiments made with this dyeing process gave favourable results in every instance. By its use a certain tone of colour was produced with 25 per cent. less ferridcyanide of potassium than by the usual process.

Experiments made to determine the best proportion in which to add the chloride of iron, showed that an addition of chloride of iron (solution of iron in muriatic acid, into which chlorine was afterwards introduced, or which, after the addition of half as much more muriatic acid as was first employed, was treated with nitric acid), equal in weight to half or three-fourths of the ferridcyanide of potassium employed, produced the greatest effect, whilst a larger quantity gave a paler colour. It is necessary to be cautious in adding the acid in this process, as less acid is sufficient here than in the usual method; tartaric acid gave the most favourable results. The ferridcyanide of potassium employed must of course contain no ferrocyanide, because, in this case, on the addition of the perchloride of iron, a precipitate of prussian blue would be formed. The compounds occurring in commerce can therefore be used only if they are quite free from admixture of this salt.—*Deutsche Musterzeit.* 1851, No. 3; *Schweiz. Gewerbeblatt*, xi. p. 119.

On Electro-plating. By E. Thomas *and* V. Dellisse.

It is known, from the experiments of Elkington and Ruolz, that all silver salts do not deposit a continuous coating of silver upon the objects to be plated. The conditions found to be necessary by these observers are—

1. The requisite conductibility of the bath.
2. That nothing but silver should be deposited during the action of the galvanic current.
3. That the bath should not attack the metal to be silvered.
4. That the liquid should be alkaline.

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Bouilhet has lately added a fifth to these conditions, according to which the bath must contain a double salt of oxide of silver and fixed alkali. These conditions are only answered by two sets of salts, the cyanurets and hyposulphites. Elkington has already stated that the double compounds of ammonia and silver are of no use for silvering.

The authors have now once more worked through these salts, and have found, of course, that most of them are not proper for the purpose; but that a bath consisting of a solution of double sulphurous acid and acid hyposulphite of ammonia of 8°, in which oxide of silver, or an insoluble silver salt, such as chloride of silver, has been dissolved, serves best.—*Comptes Rendus*, xxxiv. p. 556.

Lithographic Ink. By M. Weishaupt.

40 parts yellow wax.
10 parts mastic.
28 parts gum-lac.
22 parts Marseilles soap.
9 parts lamp-black.

The wax is to be heated until its vapour kindles on coming in contact with a burning match; it is then removed from the fire, and the soap, gum-lac, and mastic are added to it in small portions. The flame is then extinguished, and the lamp-black perfectly incorporated with it. It is again heated until its vapour can be ignited, when it is removed from the fire, and after the flame has been extinguished, it is poured upon a stone. The mass is then cut into pieces.—*Polyt. Central Blatt.*, 1851, p. 372.

PROCEEDINGS OF SOCIETIES.

British Association for the Advancement of Science.—Meeting held at Belfast, September 1st, 1852.

On the Composition and Microscopic Structure of certain Basaltic and Metamorphic Rocks. By Dr. Andrews.

If a thin splinter of basalt is viewed by reflected light in the field of a good microscope, it appears to consist of a semi-transparent granular mass, interspersed occasionally with fragments of opake crystals, some of which have a highly metallic lustre and dark colour, while others, from their cubical form and yellow colour, are easily recognised as iron pyrites. On further examination of the black crystals, the triangular facets of the regular octahedron, often marked with striæ, may frequently be seen; in short, they exhibit all the external characters of the magnetic oxide of iron. The semi-

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transparent portion, which forms the great mass of the stone, evidently consists of two distinct minerals. One has a resinous lustre, and very closely corresponds in microscopic characters to crystallized augite; the other is colourless, with a glassy lustre, and might be referred to some varieties of zeolite.

Thus, by simple inspection of the basaltic rock, without the application of any chemical test, it may be proved that it contains at least four distinct minerals:—1st, the colourless glassy mineral; 2ndly, augite; 3rdly, magnetic oxide of iron; 4thly, iron pyrites. These remarks refer to the compact varieties of basalt, which are free from cavities and imbedded zeolites.

The metamorphic rock of Portrush—an indurated clay containing the characteristic fossils of the lias formation, and in external characters resembling to some extent Lydian stone—exhibits under the microscope a very different appearance. The mass of the stone is seen to be formed of a semi-transparent paste of homogeneous structure, everywhere thickly studded with innumerable microscopic cubes of iron pyrites. These crystals are very perfectly formed, but so minute that I have frequently counted twenty of them in the space of $\frac{1}{100}$dth part of an inch square; on measurement, each side of the crystal is about $\frac{1}{2000}$dth of an inch. If we reduce a portion of any of these rocks in a porcelain mortar to a tolerably fine, but not impalpable powder, and pass a magnet several times through the powder, magnetic particles will be found adhering to the magnet in greater or less abundance, according to the nature of the rock. On removing these magnetic bodies from the magnet, which, for convenience, ought to terminate in a point, and placing them in the field of a microscope, they exhibit distinct polarity, and all the other characters of the magnetic oxide of iron. This simple microscopic test is by far the best means of detecting the presence of the magnetic oxide of iron in rocks; and it is remarkable how very closely the external characters of this mineral, when thus extracted, agree, whatever the rock may be from which it has been obtained. It may be separated in this way from all the varieties of basalt which occur in the north-east of Ireland, but in some varieties in greater abundance than in others. The largest quantity I have observed occurs in a dyke which traverses the clay slate of Down. It may also be extracted from granite, primitive limestone, hardened chalk, magnesian limestone, and many metamorphic rocks. In short, it is one of the most widely-diffused minerals in nature, being present in almost every rock which exhibits evidence of igneous action. In roofing-slate, serpentine, and marble a doubtful trace however only could be detected.

I have now to give an account of another very common, although far from abundant constituent of many igneous rocks, the existence of which has not been hitherto even suspected. It is well known that metallic iron is one of the rarest of terrestrial minerals. Alloyed with a small quantity of nickel, it is a common and characteristic constituent of aërolites; and the large isolated masses of the same alloy

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which have occasionally been discovered in different parts of the world are, with the highest degree of probability, also supposed to be of meteoric origin. But samples of native iron, not of meteoric origin, are of very rare occurrence, and some mineralogists consider the statements which have been made on this point to be far from established. In the 'Tableau Comparatif,' published in 1809, Hauy has the following remarks on this very subject:—"The existence of native iron can no longer be disputed, though this mineral has only in a very few instances been found in the interior of the earth. It occurs in small masses coated with oxide of iron, or some other ore of the same metal. Karsten has described a specimen of this kind from Kamsdorff, in Saxony, and M. Schreiber another from the mountain of Ouille, in the department of Isere. Native volcanic iron has also been discovered by M. Massier in a ravine formed by the action of rain-water in the scoria and lava of the mountain of Graveneire, in the Puy de Dome. In addition to these cases cited by Hauy, I have not been able to find more than three or four others in which native iron has been supposed to be discovered.

At Canaan, in Connecticut, it is said to have been found in a vein or plate two inches thick, attached to a mass of mica-slate; and it has also been observed in the form of fine granules in the same rock. On the other hand, from the abundance of old pieces of iron, especially where mining operations are carried on, some observations of this kind must be regarded as of doubtful authority; as, for example, the statement of Kramer, that a mass weighing 1 lb. was obtained in the mine of Hackenburg. On this point I have been favoured with the following remarks by Professor Rose:—"You are probably aware that metallic iron has been found in the auriferous and platina sands of the Ural mountains. My brother has also found it in them. But, on this subject, he makes the following observations in his travels to the Ural, the Altai, and the Caspian Sea:—Whoever has observed the manner in which the sands containing gold and platina are washed, can have no doubt as to the origin of the little scales which have been found in these sands. We may certainly assume, without hesitation, that they are small fragments of iron which have been abraded from the iron stirrers during the washing of the gold. On examining the washed gold from Schabrowskai, I have found several such little fragments."

Considering the many points of resemblance between basaltic rock and meteoric stones, and the very frequent occurrence of metallic iron alloyed with metal in the latter, I considered it not improbable that metallic iron might also be found in the former; and after several unsuccessful attempts, I at last succeeded in detecting it by a rather novel test. The stone is first reduced to powder in a porcelain mortar, carefully avoiding the use of metallic tools in any part of the operation; the magnetic portions are then removed as in the process for separating the oxide of iron, and placed in the field of the microscope. While in the field they are moistened with an

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acid solution of sulphate of copper, which produces no change upon the pure oxide, but immediately indicates the presence of the slightest trace of the pure metal by a deposition of metallic copper. On making the experiment, an occasional deposit of copper occurred in irregular crystalline bunches, perfectly opake, and with the characteristic colour and lustre of the precipitated metal. On placing a minute fragment of copper close to one of these deposits, and adding gradually nitric acid to the liquid, they both began to dissolve, and at the same moment, with the evolution of gas. But indeed the great brilliancy and freshness of the metallic surface were too distinct to admit of any doubt, even on the most superficial examination. With neutral solutions of the copper salt this deposit very rarely occurs; indicating either that the iron is covered with a film of oxide, or that it is analogous in properties to the meteoric alloy, which precipitates copper from acid, but not from neutral solutions. If, instead of the copper solution, dilute sulphuric acid be added to the magnetic particles, a slight effervescence, at particular points, will frequently indicate the presence of this metal; and on adding the solution of copper, while the disengagement of gas continues, it will be suddenly arrested, and a bright deposit of metallic copper will appear at the same place. The deposits of copper are sometimes in the form of small compact niches, but more frequently they assume the figure of a ring, embracing partially a crystal of the oxide. They thus enable us to form a pretty clear conception of the form of the iron with which they have been deposited. I have never, by the most careful examinations, been able to distinguish the metallic lustre of the iron itself, either from the very minute size of the particles, or perhaps from the surface not being brilliant. The largest deposit of copper which I ever obtained was little more than one-fiftieth of an inch in diameter; in general they were much smaller even than that magnitude. By far the most abundant indications of metallic iron were obtained from a coarse-grained variety of basalt, which constitutes the hill of Slievemish, in the county of Antrim, and is also found at the Maiden Rocks, and in other localities. From 100 grs. of this rock, three or four deposits of copper can usually be obtained. With the compact fine-grained basalt of the Giant's Causeway, I have also occasionally obtained a deposit of copper, but far less frequently than with the Slievemish basalt. I have also obtained distinct indications of the presence of iron in the indurated lias slate of Portrush and in the trachyte of Auvergne.

This experiment is, of course, liable to the ambiguity that nickel and cobalt, in a state of very fine subdivision, also precipitate copper, but the extreme improbability of either of these metals being present is so great, that this objection scarcely weakens the conclusions at which I have arrived.

The origin of the metallic iron, in this diffused state, is an interesting subject of speculation. May it not be due to the reducing action of such gases as hydrogen or carbonic oxide, while the basaltic rock is still in a state of ignition?

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Note on the Oil of the Squalus maximus.
By Prof. Ronalds.

The basking shark, commonly called Sun-fish by the fishermen, is taken in considerable numbers off the bay of Galway in the spring of the year. The liver of the fish, from which the oil is obtained, is removed, and the carcase allowed to float, being too bulky for the boats employed in the fishery. The liver affords about 80 per cent. of oil, and that of a single fish will often yield as much as 120 gallons. The oil is extracted from the liver by the fishermen, on a small scale, by melting in iron pots over a peat fire. It possesses a light yellow colour and a fishy disagreeable smell when freshly prepared, which it loses by exposure to the air and light. The oil is remarkably light, its specific gravity ranging between 0·870 to 0·876, a property which should render it valuable as a lubricating agent, the power of diminishing friction in oils being, it is said, in the inverse proportion to the specific gravity. The oil does not solidify by cold several degrees below the freezing-point. It burns in Argand lamps with an exceedingly brilliant flame, quite equal to that of the vegetable oils in general use, and does not clog the wick, as is the case with most inferior oils.

When heated, it boils at a temperature somewhat below that of boiling mercury, and a clear yellow oil distils over, diffusing a powerful smell of acroleine, and thus indicating the presence of glycerine in the oil, but affording to water no evidence of the formation of sebacic acid, a fact which has led to the supposition that the oil must contain some other than the ordinary modification of oleic acid.

The composition of the crude oil was found (the mean of three analyses) as follows:—

Carbon	82·77
Hydrogen	12·96
Oxygen	4·27

and is somewhat remarkable for the large amount of carbon and very small amount of oxygen which it shows.

A considerable quantity of iodine is also contained in the oil, but this has not yet been accurately estimated.

A numerous series of experiments were made to isolate the oleic acid of this oil, but the results were not sufficiently satisfactory to warrant the author in establishing a formula or atomic weight for the acid. All the analyses of the acids, prepared and purified by different processes, gave results in which the per-centage of carbon exceeded very considerably the quantity contained in oleic acid, thus far corroborating the assumption that some other than oleic acid is contained in the oil; but no two processes as yet employed appeared to afford the same result, and the salts of baryta obtained from the acid were obviously mixtures, and not combinations of one and the same acid.

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THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Mercurial Compounds of the Alkaloids.
By Dr. HINTERBERGER.

Hydrargyro-chloride of Narcotine, $C^{48}\ H^{21}\ NO^{14}$, HCl, HgCl.—If an alcoholic solution of narcotine, which has been acidulated with muriatic acid, be added to a watery solution of perchloride of mercury, a white precipitate is obtained. If this, after being dried on the water-bath, be dissolved without heat in 2 vols. of alcohol to which 1 vol. of concentrated muriatic acid has been added, and if into the clear solution so produced small portions of distilled water be poured until the turbidity produced by every addition of water no longer disappears on stirring, and this slight turbidity be got rid of by the application of a gentle heat, the hydrargyro-chloride separates in small crystals of a perfectly white colour. As this compound is insoluble in water, it can be washed therewith. The analysis of the hydrargyro-chloride of narcotine, dried at 212°, gave the following results:—

Carbon	43·64	42 =	252·0	44·15
Hydrogen	3·906	22	22·0	3·86
Nitrogen	..	1	14·0	2·44
Oxygen	..	14	112·0	19·62
Mercury	18·02	1	100·0	17·52
Chlorine.....	..	2	70·8	12·41

Wertheim has shown, that besides the narcotine discovered by Blyth, two other bases homologous with it occur. He calls one of these, characterized by the expression $C^{48}\ H^{27}\ NO^{14}$, propylo-narcotine, because when treated with hydrate of potash at a temperature of 392°, it furnishes propylamine; and the other, which yields methylamine by the same treatment, and the formula of which is $C^{44}\ H^{23}\ NO^{14}$, methylo-narcotine. He considers the narcotine of Blyth to be æthylo-narcotine, and expresses his conviction that it will furnish æthylamine by decomposition with hydrate of potash. If $C^{2}\ H^{2}$ be deducted from the methylo-narcotine, the formula of the narcotine analysed by the author is obtained:—

$C^{44}\ H^{23}\ NO^{14}$, methylo-narcotine.
$C^{2}\ H^{2}$ — 2 equivs. of carburetted hydrogen.

$C^{42}\ H^{21}\ NO^{14}$, narcotine Narc.

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The interesting relations which exist between the various known bases homologous with the narcotine of Blyth will be best seen from the following equations:—

Narcotine ..... $C^{42}H^{21}NO^{14} = \overset{+}{N}arc.$

Methylo-narcotine ..... $C^{44}H^{23}NO^{14} = \overset{+}{N}arc. + 2CH.$

Æthylo-narcotine (narcotine of Blyth) $C^{46}H^{25}NO^{14} = \overset{+}{N}arc. + 4CH.$

Propylo-narcotine..... $C^{48}H^{27}NO^{14} = \overset{+}{N}arc. + 6CH.$

The narcotine characterized as $\overset{+}{N}arc.$ is distinguished from the three other bases, just as ammonia is distinguished from methylamine, æthylamine and propylamine:—

Ammonia $= NH^3.$
Methylamine $= NH^3 + 2CH.$
Æthylamine $= NH^3 + 4CH.$
Propylamine $= NH^3 + 6CH.$

This kind of narcotine was procured by the author from M. Redtenbacher, who obtained it from the manufactory of Mr. Morson in London. The crystals were colourless prisms of the thickness of the shaft of a raven's feather, were throughout of the length of half an inch or more, and exhibited smooth shining faces.

Hydrargyro-chloride of Brucine, $C^{46}H^{26}N^2O^8$, HCl, 2HgCl.—This compound is obtained by pouring a concentrated alcoholic solution of corrosive sublimate into a solution of muriate of brucine in strong alcohol. If to the resulting mass of small acicular crystals some alcohol and concentrated muriatic acid be added, and the whole be slightly warmed, a clear solution is obtained, from which the compound separates, during gradual cooling, in the form of rather long perfectly colourless needles. These crystals are put upon a filter, washed, first with plenty of water, and afterwards with strong alcohol, and then dried on the water-bath. Analysis gave—

Carbon	39·31	46	= 276·0	39·36
Hydrogen	4·00	27	27·0	3·85
Nitrogen	..	2	28·0	3·99
Oxygen	..	8	64·0	9·12
Mercury.....	27·84	2	200·0	28·52
Chlorine.....	..	3	106·2	15·16

It is composed of 1 equiv. of muriate of brucine and 2 equivs. of perchloride of mercury. This expression confirms the accuracy of the formula $C^{46}H^{26}N^2O^8$, deduced by Dollfuss and Anderson from their analyses of brucine compounds.

Hydrargyro-chloride of Berberine, $C^{42}H^{18}NO^9$, HCl + HgCl.—In order to procure this compound well-crystallized, a solution of berberine in plenty of strong alcohol, and containing an excess of muriatic acid, is mixed with an alcoholic solution of perchloride of mercury acidified with muriatic acid, at a boiling temperature, when the liquid will remain clear; but during the process of cooling the

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compound soon begins to separate in the form of beautiful, bright yellow, shining, silky needles. The mother-liquor, which still remains yellow, is now poured off from the crystals, and these are washed first with alcohol, then with water, and lastly again with alcohol. The hydrargyro-chloride of berberine remains unaltered in the air, does not change at 212°, and is soluble in a very large quantity of hot water. The analysis of the compound, dried at 212°, gave—

Carbon	47·10	47·09	42 =	252·0	47·740
Hydrogen	3·53	3·66	19	19·0	3·599
Nitrogen.....	..	..	1	14·0	2·650
Oxygen	..	..	9	72·0	13·640
Mercury.....	20·17	16·69	1	100·0	18·950
Chlorine.....	..	..	2	70·8	13·421

The difference between the quantity of mercury found and calculated induced the author to recrystallize this hydrargyro-chloride of berberine in order to obtain it as pure as possible. The crystals were therefore dissolved in hot distilled water; longer and larger crystals were soon formed in the solution, which however had a different composition, as the following analysis shows:—

Carbon	37·700	42 =	252·0	37·990
Hydrogen	2·866	19	19·0	2·865
Nitrogen	..	1	72·0	2·100
Oxygen	..	9	72·0	10·860
Mercury	30·420	2	200·0	30·160
Chlorine.....	..	3	106·2	16·025

This compound is therefore $C^{42}H^{18}NO^9+HCl+2HgCl$. Thus by the recrystallization of the hydrargyro-chloride of berberine of the composition $C^{42}H^{18}NO^9+HCl+HgCl$, a mercurial compound is obtained, which contains 2 equivs. of perchloride of mercury to 1 equiv. of muriate of berberine.

Hydrargyro-chloride of Caffeine, $C^{16}H^{10}N^4O^4+2HgCl$.—Caffeine is known to have weak basic properties, and to furnish very unstable salts with acids. A solution of its muriate forms with chloride of platinum a double compound of the constitution $C^{16}H^{10}N^4O^4+HCl+PtCl^2$.

If to a concentrated alcoholic solution of caffeine, acidified by an excess of muriatic acid, an aqueous solution of corrosive sublimate be added, so large a quantity of small acicular crystals immediately separates, that the entire liquid stiffens into a gelatinous mass. By the application of a gentle heat, the crystals are again dissolved, and after this, long, shining, silky crystals shoot out, which are partly grouped in a stellate form. They were washed with water, alcohol, and lastly with æther, and dried at 212°. Analysis gave—

Carbon.....	20·45	16 =	96·0	20·65
Hydrogen	2·14	10	10·0	2·15
Nitrogen	..	4	56·0	12·08
Oxygen	..	4	32·0	6·88
Mercury	42·61	2	200·0	43·00
Chlorine	..	2	70·8	15.24

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This is the compound obtained by Nicholson by adding corrosive sublimate to an aqueous solution of caffeine.

No double salt of the chloride of caffeine with the perchloride of mercury, similar to those formed by the other alkaloids, could be obtained. The analysis of the perchloride of mercury and caffeine was therefore interesting, because it afforded an opportunity of ascertaining that Bunsen's method of determining the mercury merits the preference over that proposed by Nicholson, on account of the accuracy of the determination of the hydrogen.

Hydrargyro-chloride of Cinchonine.—From the analysis of this substance the author derived the formula $C^{38}H^{22}N^2O^2+2HCl+2HgCl$, which is perfectly analogous with that of the double platinum compound described by Laurent. The cinchonine employed is to be recrystallized, and the crystals first formed by this process are to be used in preparing the double compound. On mixing an alcoholic solution of the recrystallized cinchonine with an alcoholic solution of perchloride of mercury, the whole fluid does not solidify into a mass of acicular crystals, as is the case when commercial cinchonine is employed; even after the lapse of twenty-four hours no crystals have separated. It is only on the addition of water that a white precipitate is obtained, which becomes crystalline by exposure to cold. The analysis of the hydrargyro-chloride of cinchonine thus obtained showed that the author had to do with a mixture of the substances lately found by Hlasiwetz in commercial cinchonine.

Hydrargyro-chloride of Atropine could not be procured in a form suited for analysis. Muriate of atropine certainly gives a white precipitate with perchloride of mercury, but this soon cakes into a plaster-like mass. This inconvenience could not be got over by making the mixture at a very low temperature.

Several experiments made with atropine showed that Planta was perfectly right in stating that it was very difficult to obtain the salts of atropine in a crystalline form. Thus it has not been possible to prepare cyanide of atropine in a crystalline form.

If cyanogen, evolved from cyanide of mercury, be passed into a concentrated alcoholic solution of atropine, the liquid acquires a blood-red colour, but no crystals make their appearance; even after the spontaneous evaporation of the alcohol, nothing more than a syrup-like red fluid, insoluble in water, is obtained.

A watery solution of *bebeerine*, acidified with muriatic acid, gives a white precipitate with a watery solution of corrosive sublimate. This precipitate appears to be decomposed by boiling in water, as the greatest part of it separates as a green resinous mass, which adheres firmly to the vessel.

[To be continued.]

On a new Compound of Cobalt. *By* E. Saint-Evre.

When a cold concentrated solution of nitrite of potash is brought into contact with a similar solution of nitrate of cobalt, the following phænomena are observed:—Deutoxide of nitrogen is evolved, at the

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same time that an insoluble precipitate, of a peculiar yellow colour, is deposited. The liquid from which the latter has been thrown down contains a considerable quantity of nitrate of potash.

This new substance may also be produced by the two following methods:—First, by precipitating the nitrate of cobalt by potash, so as to form the blue subsalt; bringing this in contact with a slight excess of nitrite of potash, and letting fall upon it a slender stream of nitric acid by means of a pipette. In this case, the disengagement of deutoxide of nitrogen, the formation of nitrate of potash, and the production of the yellow precipitate are observed: and, secondly, by precipitating the nitrate of cobalt by a slight excess of potash, until the rose-coloured hydrate of protoxide of cobalt makes its appearance, and then passing into the resulting mass a stream of deutoxide of nitrogen. In this last case the reaction is so distinct and so prompt, that it forms a pretty experiment for the lecture-room.

This yellow body possesses the following properties:—It is of a bright yellow; its tint is so bright that it constitutes the type of yellow in the chromatic circle of M. Chevreul. It is neutral with litmus. Examined under the microscope, it consists of four-sided prisms terminated by triangular facets. It is not sensibly soluble in water, and perfectly insoluble in alcohol and æther. Sulphuret of carbon dissolves traces of it. Boiling water decomposes it, in the absence of the air, disengaging deutoxide of nitrogen. In contact with the air, the formation of vapours of nitric acid is observed, whilst the liquid becomes alkaline and acquires a rose colour. It contains ordinary nitrate of cobalt and nitrite of potash. When suspended in water, it resists the action of a current of chlorine gas for a long time. It is only by heating the mixture that it can be decomposed. Under the same circumstances, it resists equally well the action of sulphuretted hydrogen. The hydrosulphate of ammonia however causes the almost immediate formation of black sulphuret of cobalt. It evolves reddish vapours under the action of acids. A watery solution of potash precipitates hydrate of the sesquioxide of cobalt. This hydrate loses its water gradually at 212° F., only retaining 1 equiv. of it, which it parts with at a temperature above 311° F. It is also slightly soluble in hot water.

Calcined in contact with the air in a closed tube, the substance changes its colour to orange-yellow. At the same time it fuses, with disengagement of water, reddish vapours of hyponitrous acid and white vapours of nitric acid. The residue is composed of sesquioxide of cobalt and nitrite of potash. By operating in a stream of nitrogen or of dried carbonic acid, deutoxide of nitrogen is obtained in addition to the above products. Lastly, in the same circumstances, but making use of the high temperature of a charcoal fire to produce decomposition, after removing the carbonic acid by means of potash, and the deutoxide of nitrogen by sulphate of the protoxide of iron, a gaseous residue is obtained presenting the properties of nitrogen.

The author, in consequence of the unforeseen difficulties which he has met with in the quantitative determination of the potash and

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cobalt, has stopped at the following process. This process consists in boiling the substance to be analysed with pure acetate of soda, slightly acidulated, if it be alkaline, with a small quantity of acetic acid. The cobalt must then be precipitated by sulphuretted hydrogen, the sulphuret decomposed by dilute nitric acid, the nitrate of cobalt thus obtained evaporated and calcined, and the resulting sesquioxide reduced by hydrogen. It is necessary, lastly, to ascertain whether, in spite of all precautions, some sulphur, in the form of a sulphuret or oxysulphuret, does not remain in the oxide to be reduced; and if it exist, to determine its quantity in the form of sulphate of baryta, in order to deduct its weight from the total. For the quantitative determination of the potash, the cobalt must first be got rid of by precipitation in the state of sulphuret.

The results of the analysis lead to the formula—

$$N^2 O^8, CbO, KO, \tfrac{1}{2}HO.$$

We must therefore, as much in consequence of the presence of water as of the formation of sesquioxide of cobalt by calcination, double the preceding formula, which then becomes—

$$2(N^2 O^8, CbO, KO)\,HO \text{ in equivalents.}$$

By reducing the reaction to its most simple form, it may be accounted for in the following manner:—1 equiv. of nitrate of cobalt, 2 equivs. of nitric acid, and 4 equivs. of nitrite of potash contain the elements of 3 equivs. of nitrate of potash, 2 equivs. of deutoxide of nitrogen, which are evolved, and $1\frac{1}{2}$ equiv. of the yellow substance, which is precipitated, taking the quantity of water which is necessary to it:—

$$\left.\begin{matrix} NO^5\,CbO \\ +2(NO^5) \\ +4(NO^3\,KO) \end{matrix}\right\} = \left\{\begin{matrix} 3(NO^5\,KO) \\ +2(NO^2) \\ +2(NO^4, CbO, KO). \end{matrix}\right.$$

The formula given above requires—

Nitrogen	15·42	4 =	56	15·34
Oxygen.....	.. .	16	128	35·07
Oxide of cobalt	20·48	2	76	20·82
Potash	26·50	2	96	26·30
Water	..	1	9	2·47

From these facts it appears that this salt must be considered as a combination of nitric and nitrous acids united with potash, water and protoxide of cobalt. At least this is the most simple mode of stating the results.

In consequence of the beauty of its tint, and the resistance which it presents to the action of the ordinary agents of oxidation and sulphuration, the author thinks that this cobalt yellow might be advantageously employed in painting. Experiments commenced more than a year ago, the results of which are in the hands of M. Chevreul, show that it may be employed without any alteration, either by itself or mixed with other colours, both in oil and water-colour painting. Several artists have already made use of it.—*Comptes Rendus*, Oct. 16, 1852, p. 552.

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Researches on Pyroxyline. *By* A. BÉCHAMP.

We frequently encounter difficulties in preparing soluble pyroxyline. In obtaining that employed by me, I followed the process of MM. Gaudin and Mialhe. I have ascertained that if the mixture of sulphuric acid and nitre be cooled previously to the immersion of the cotton, the pyroxyline obtained is strongly fulminating, but insoluble in æther. On recommencing the same operation with the same materials, but at the temperature naturally developed by the reaction, the product obtained was both fulminating and soluble. Again, the insoluble pyroxyline formed in the first operation became soluble after being immersed in the hot mixture of the acid and nitrate.

The condition necessary for constantly obtaining soluble pyroxyline is therefore to operate whilst the mixture is hot.

When a stream of ammoniacal gas is passed, for at least half an hour, through a solution of 2 parts of pyroxyline in 30 parts of alcohol of spec. grav. 0·845, the viscous solution becomes perfectly fluid.

In this ammoniacal solution, sulphuretted hydrogen gas produces a yellow precipitate, which is insoluble in alcohol of spec. grav. 0·833 This precipitate is complex; it contains a portion which is, and a another which is not soluble in water. According to some of its reactions, I thought it like a sulphuretted compound.

When the ammoniacal solution is poured suddenly into 15 or 20 times its volume of water, a white powder, completely insoluble in water, is precipitated; it is not altered by remaining for forty-eight hours in water. Its properties are as follows:—

Dried at 68° F. *in vacuo* over sulphuric acid, it is very persistent. It is light, inodorous and tasteless. It becomes electric by friction. Heated in a tube, it does not fulminate so soon as pyroxyline; it evolves nitrous vapours, and leaves a residue of carbon. Heated with fuming muriatic acid, it is gradually dissolved, disengaging chlorine in abundance. Concentrated sulphuric acid dissolves it, without apparent disengagement of gas. The nitro-sulphuric mixture does not appear to produce any change in it. I have not yet ascertained whether or not the pyroxyline was regenerated.

The water in which the precipitation takes place contains nitrate of ammonia, but very little organic matter. This fact deserves attention. The elementary analysis shows, in fact, that the new combination only differs from pyroxyline by containing 1 equiv. less nitric acid.

I have ascertained that the new substance is constant in its composition. I have analysed the product immediately after its precipitation, and also after forty-eight hours' contact with water. The composition did not vary.

In six analyses for the determination of the carbon and hydrogen, and three others in which I determined the nitrogen by the process of M. Dumas, I obtained concordant results; the average of the four elements is in hundredths,—carbon, 28·216; hydrogen, 3·575;

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nitrogen, 10·777; oxygen, 57·432. The substance had been dried at 212° F. Taking into consideration the formation of nitrate of ammonia in the reaction, and admitting the formula attributed to pyroxyline by M. Pelouze (Comptes Rendus, xxiv. p. 2), namely $C^{24} H^{17} O^{17}, 5NO^5$, the substance examined by me would be formed according to the equation—

$$C^{24} H^{17} O^{17}, 5NO^5 + NH^3 + HO = NO^5, NH^4 O + C^{24} H^{17} O^{17}, 4NO^5.$$

If we take this last formula for that of the new compound, its theoretical centesimal composition is,—carbon, 28·070; hydrogen, 3·315; nitrogen, 10·916; oxygen, 57·699.

Between 68° and 212° F., 100 parts of the substance lost, by the average of two determinations, 1·727 of water. This number, supposing H=1, represents 9·015 of water for the quantity of substance expressed by the formula $C^{24} H^{17} O^{17}, 4NO^5$, that is to say, 1 equiv. of water. The formula of the new substance, at the temperature of 68° F., is therefore $C^{24} H^{17} O^{17}, 4NO^5, HO$, or, dividing it by 2—

$$C^{12} H^9 O^9, 2NO^5 = C^{12} H^9 (NO^4)^2 O^{11},$$

that is to say, the formula of cane-sugar, in which $2NO^4$ take the place of 2H.

Conclusion.—Several formulæ are attributed to pyroxyline. The new compound, by its composition as well as by the circumstances of its formation, confirms the formula of M. Pelouze.

The following is the molecular formula which I propose for pyroxyline:—

$$C^{24} H^{17} X^4 O^{21}, NO^5 *;$$

that of the new compound, dried at 68° F., being $C^{24} H^{17} X^4 O^{24}, HO$; and that of the same, dried at 212° F., $C^{24} H^{17} X^4 O^{21}$.

I have already commenced some experiments on the nitrated products insoluble in water which result from the action of the nitrosulphuric mixture on glucose, dextrine, gum, &c.—*Comptes Rendus*, Oct. 4, 1852, p. 473.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Composition of the Substances employed by the Chinese in the Decoration of Porcelain. *By* MM. Ebelmen *and* Salvétat.

In a former memoir†, the authors made known the substances used by the Chinese in the manufacture of porcelain. They now communicate their investigation of the various colouring matters employed in the decoration of these potteries.

The special results of these investigations show—

1. That the Chinese have only a small number of the colours

* $X = NO^4$. † Chem. Gaz., vol. ix. p. 390.

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known as *muffle colours* (colours which fuse at a low temperature in comparison with that at which the porcelain is baked).

2. That the palette of the Chinese is not composed of true colours, but rather of enamels; these enamels are glasses, that is, compounds of oxide of lead and alkalies, variously coloured by a few parts per cent. of colouring oxides dissolved in them.

3. The composition of this glass is but little variable; it is always weakly coloured; and it is even this weakness of tone and liveliness of tint which furnish the means by which the Chinese produce harmony and variety of colour upon their porcelain.

4. These enamels are coloured by oxide of cobalt, oxide of copper and gold; therefore by substances which are all readily soluble in the fluxes, the preparation of which is very simple.

In addition to these, antimony is employed for yellow, tin and arsenic acid for opake white. The Chinese mix these substances with the enamels, and these latter with one another, to produce very various shades of colour. Their compound colours however are always referable to five colouring elements,—blue, oxide of cobalt; blue or green, oxide of copper; rose, gold; yellow, oxide of antimony.

If we add to these the very impure oxide of cobalt, which always gives a blue under the glazing; the same oxide, which is mixed with white lead to be burnt upon the glazing, and then furnishes a black; oxide of iron mixed with white lead or flux, to produce various shades of red; lastly, gold, which is rendered fit to be melted upon the glazing of the porcelain by being mixed with a tenth part of white lead,—we have all the means at the command of the Chinese decorator of porcelain.

The enamels are laid on with water, or sometimes with solution of gum or glue.

The authors attribute the circumstance, that glassy materials, such as these enamels, can be laid upon Chinese porcelain, without removing the glazing, to the peculiar composition of the latter. The composition of this was communicated in their previous memoir. A pure felspar glaze does not suit enamel. The authors attribute the peculiar appearance which distinguishes the Chinese and Japanese porcelain from European entirely to the composition of the glaze.

There is yet another kind of decoration employed for Chinese stone-ware or porcelain, in which the objects are entirely coloured either with the pencil or by dipping. This mode of colouring will be considered by the authors in a third memoir.

The processes employed in Europe in the decoration of porcelain are shortly as follows:—Sometimes variously-coloured pastes are employed, sometimes the colouring matter is introduced into the glaze, and sometimes the colours are laid on the surface of the white porcelain. The two first methods require the application of as high a temperature as that necessary for the baking of the porcelain itself. The colours so employed are therefore called *strong fire colours* (*couleurs de grand feu*). But when, on the other hand, the colours are laid on the surface of the porcelain, they require for

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their vitrification a much less elevated temperature than the preceding. These colours are called *muffle colours* (*couleurs de moufle*). They are the only colours which have hitherto presented, for painting on porcelain, resources comparable to those furnished by painting in oil; and it is with these colours, such as they have become by gradual improvement in the course of the last fifty years, that several works of the great masters have been reproduced on porcelain with the greatest exactitude.

The colours employed by the Chinese may also be divided into two similar classes of *strong fire* and *muffle colours*.

Some of the Chinese *strong fire colours* have not yet been reproduced on the European porcelains. They are extremely delicate, and often so beautiful that it is a matter of the greatest interest to be able to imitate them. The authors have nearly terminated their analyses of these colours, but in the present memoir they devote their attention exclusively to the muffle colours.

The materials examined by the authors are derived partly from the collection formed in China by Father Ly, partly from the collection of the École des Mines, and partly from that of the Musée Céramique. These colours are particularly employed at King-teching. The authors also made use of the colours employed at Canton and in its neighbourhood, which were collected partly by M. Itier, and partly by Mr. Rutherford Alcock, the English consul at Shanghai.

M. Itier took his colours from the table of a Chinese painter who was engaged at the time in the decoration of porcelain. They offer a remarkable character of authenticity. Those sent by Mr. Rutherford Alcock to the Musée Céramique de Sèvres, appear to be a repetition of the collection exhibited last year at the Crystal Palace.

In Europe, and especially at Sèvres, the colouring metallic oxides are mixed with a flux, the nature of which varies according to that of the colour. The most usual is the *gray flux* (*fondant aux gris*), which serves for gray, red, blue and yellow, and is formed by melting together—

Minium	6 parts
Quartz sand	2 ...
Glass of borax	1 ...

The colours are generally obtained by mixing together 3 parts of flux with 1 part of the metallic oxide, so that the composition may generally be expressed as follows:—

Silica	16·7
Oxide of lead	50·0
Borax	8·3
Colouring metallic oxide	25·0

Sometimes the oxide and flux are melted together, or calcined before being employed; sometimes they are simply mixed together. If the colour be produced by a combination of the oxide with the flux, they must be melted together before use, in order that the colour may possess the proper tone. If, on the other hand, the

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colour be proper to the oxide, it need only be mixed with the flux, and must not be melted with it before use, as this double fusion frequently changes the colours. All the colours must melt at the same time, and present, after baking, a sufficiently uniform gloss.

These conditions are not fulfilled by the Chinese colours. Some of them are brilliant, well-vitrified, and often laid on so thickly that they project from the surface. This is the case with the blues, greens and yellows, and with the rose colour obtained from gold. Others, such as the iron-reds and the blacks, are almost always less thickly laid on, less perfectly vitrified, and generally dull and muddy.

The Chinese paintings are always distinguished from ours by a very distinct character,—the figures and other objects are not properly painted, but outlined with a black or red line; the tints are never lowered; the colours are laid on uniformly, and the painter then goes over this ground, either with the same or another colour, so as to produce a motley work; but the mixture of the colours on the palette, which constitutes the greatest resource of our painters, appears not to be employed by the Chinese. The appearance of their paintings, when closely examined, reminds one of the mosaic church windows, which were fabricated with so much art in the thirteenth century, and in which the entire design, and all the forms of the figures and accessories, were only produced by red or brown lines drawn upon fragments of white or coloured glass.

From the thickness with which the Chinese lay on their colours, and their slight intensity, we may arrive at the conclusion, that these colours contain far smaller quantities of metallic oxides than those employed in Europe. The colours are rather *enamels*.

The names applied to the samples investigated by the authors were attached to them in Chinese characters, and have been translated by M. Stanislas Julien.

The substances examined included some primary substances employed in the fabrication of the colours. As to the colours, some, not having received any mechanical preparation, are in larger or smaller fragments, and are designated by the generic term *Seng*; the others are pulverized, and completely prepared for painting; these are included under the generic name *Si*.

1. *Crude Substances and isolated Oxides.*

Sy-chy-mo (fine stone powder).—This is a siliceous, amorphous, grayish powder, becoming white on burning. Some minute spangles of mica are visible in it with the lens. It is infusible before the blowpipe, and presents all the properties of the siliceous sands employed in the fabrication of glass. Analysis gave—

Loss by heat	0·40
Alumina	0·15
Peroxide of iron	0·45
Lime and magnesia	traces
Silica	98·70

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The *Sy-chy-mo* is probably the substance employed by the Chinese in the fabrication of their coloured enamels. They use it also, according to Father Ly, to harden colours which are found too fusible.

Yuen-fong (lead-meal).—Four different samples of this material were ascertained, on analysis, to consist of white lead. This white lead is completely soluble in dilute nitric acid, with the exception of a trace of silica; it is free from oxide of copper and acetate of lead.

Fan-hong is a light red powder, which stains the fingers, is soluble in boiling muriatic and sulphuric acids, and not readily attacked by nitric acid. The Chinese use this substance mixed with some white lead, or silicate of oxide of lead, for the production of red. It appears that the Chinese prepare this red colour by the calcination of some natural deposit of yellow ochre, although this cannot be determined with certainty, as Father d'Entrecolles has already informed us that the Chinese are acquainted with copperas (which they call *Tsao-fan*), and also with the residue of its distillation. The authors have examined two different samples, one, *a*, from the collection of the École des Mines, the other, *b*, from that of the Musée Céramique. Their composition is—

	a.	*b.*
Moisture	1·00	1·20
Silica	3·90	3·12
Alumina	trace	3·00
Oxide of iron	95·00	92·14
Lime	trace	trace
Magnesia	trace	trace
Loss	0·10	0·54

Thsing-hoa-liao.—The École des Mines possesses eight different specimens, three of first, two of second and three of third quality. All the samples consist of the same material in various states of preparation. One of the three specimens of first quality presents the material in its rough state, as first taken from the mine; the others are in various states of purification. The collection of the Musée Céramique only possesses one substance similar to the *thsing-hoa-liao*; it was sent by Father Ly under the name of *ching-lan*, which he translates *deep blue*. The collection sent by Mr. Rutherford Alcock contains several bulky specimens of this mineral, which is a peculiar kind of oxide of cobalt. It forms irregular fragments, containing hollow spaces, of a deep brown colour with a greenish tinge, and furnishes a brown powder which stains the fingers. On being heated, it evolves water, and after long-continued calcination acquires more of a greenish hue. At a red heat it suffers a loss of 20 per cent. in weight. It contains oxides of manganese and cobalt, but these two oxides do not form the whole of its mass. Muriatic acid leaves a residue of silicate of alumina. During solution in muriatic acid, chlorine is evolved, and the solution contains the metals. Analysis gave—

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	Rough mineral.	Prepared mineral.
Loss (water and oxygen)	20·00	4·00
Silica (insoluble residue)	37·46	27·00
Oxide of copper.....	0·44	2·00
Alumina.....	4·75	65·00
Oxide of manganese	27·50	
Oxide of cobalt	5·50	
Oxide of iron	1·65	
Lime	0·60	1·00
Magnesia	trace	trace
Arsenious acid	trace	1·00
Oxide of nickel and sulphur	trace	

The powder of this mineral melts with borax before the blowpipe into a rose-coloured globule, which however has a tinge of blue from the oxide of cobalt. Laid with the pencil upon a piece of burnt Sèvres porcelain, then glazed and exposed to the strong fire, it furnished a blue tint in the thinner parts, becoming greyish in the stronger shades. The Chinese employ this substance for the production of blue pictures under the glazing; and if it be rich enough in oxide of cobalt, also in the preparation of the blue muffle colours; and lastly, in the production of black. All the samples came from the province *Yun-Nan*, where the ore is dug from the summit of a mountain. Before use, it is roasted and pounded. The same statement has already been made by Father d'Entrecolles.

2. *On the rough and prepared Colours.*

The collections of colours examined by the authors nearly always contain the colours both in the rough state and mechanically prepared and fit for use. This mechanical preparation is sometimes the only difference between the rough and prepared colours; in other cases, during the trituration of the substance, a portion of *yuen-feng* or *sy-chy-mo* is added to it; the former when it is desired to render the colour more fusible, the latter to produce a contrary effect.

The rough colours are generally irregular glassy fragments, sometimes transparent, sometimes opake. They have all the same colour if the colour be simple, but possess a varied coloration if the colour can only be produced by the mixture of two or more different colours. The proportions in which *yuen-feng* is added to those colours which require its addition, are very various even for the same colour. This must, in fact, be the case in a country where all the primitive colours coming from distant districts cannot be prepared by the same manufacturer, and where the temperature to which the paintings are exposed depends entirely on the will of the decorator.

The following may be said of the Chinese porcelain colours in general. They are very slowly dissolved in cold, but readily in hot acids. The solutions contain oxide of lead, alkali and the colouring oxide. Silica is separated, which, if muriatic or nitromuriatic acids have been employed, is mixed with chloride of lead. The readiness with which they are dissolved varies according to the nature of the colouring oxide.

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Moist air acts slowly upon these colours when reduced to a fine powder; by the action of the atmospheric carbonic acid, carbonate of lead is formed, which is dissolved with effervescence by diluted nitric acid.

1. *Whites.*

The Chinese have several kinds of whites, which are distinguished under the denominations of first, second and third quality, according to their beauty. The authors have examined the following kinds, contained in the collection at Sèvres:—

Po-ly-pé, literally glass-white of first quality.

Chang-pé, white of second quality.

Pou-pé, white of third quality.

The other rough (*seng*) and pulverized (*si*) whites appeared to possess exactly the same properties as the above, and were therefore not analysed by the authors. They are—

Chang-yan-pé, superior European white.

Sué-pé, snow-white of third quality.

Yan-yué-pé, European moon-white.

The last-mentioned, which is a white with a slight greenish tinge, is a mixture of one of the preceding whites with one of the transparent greens, which will be hereafter referred to.

Seng-po-ly-pé, or white of the first quality, requiring no addition of *yuen-feng*.—This white consists of fragments of various kinds, some opake, others opaline, and others of a grayish bullate appearance. All give a colourless powder. The opacity arises from arsenic acid. Analysis gave—

Moisture	0·40
Silica	37·00
Oxide of lead	44·39
Arsenic acid	6·00
Alumina	0·27
Oxide of iron	0·28
Lime	0·75
Magnesia	traces
Potash	9·50
Soda	0·05
Oxide of copper	traces

Seng-chang-pé, or white of second quality, not requiring *yuen-feng*.—It has the same appearance as the preceding, and gave the same elements, but in different proportions. Analysis gave—

Humidity	0·50
Silica and oxide of tin	37·50
Oxide of lead	50·94
Arsenic acid	5·00
Alumina	0·15
Oxide of iron	0·30
Lime	0·60
Magnesia	traces
Potash	3·43
Soda	0·34
Oxide of copper	traces

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This composition differs greatly from the preceding. The proportion of alkali is only a third of that in the *po-ly-pé* white. The difference would however probably be less if the colour were homogeneous; but the substance consists of various fragments, some of which are opake and appear to be richer in lead; the others grayish, and probably containing no arsenic acid.

Seng-pou-pé, or white of third quality.—For use, 1 lb. of it is mixed with 12 oz. of *yuen-feng*. This also contains the opake and opalescent masses described above as constituting the *po-ly-pé*; but they are here intimately mixed with a grayish sandy substance, which appears to be the powder of the stone *sy-chy-mo*, previously mentioned.

The opake fragments contained arsenic acid and 38 per cent. of silica, which agrees with the quantity contained in the *po-ly-pé* and *chang-pé* whites. The grayish powder, isolated as completely as possible from the opake fragments, was analysed separately by the same processes as those followed in the treatment of the other whites. The analysis gave—

Humidity	0·25
Silica	70·60
Oxide of lead	23·70
Arsenic acid	1·50
Alumina	0·42
Oxide of iron	0·35
Lime	0·23
Potash	4·00
Soda	traces
Oxide of copper	traces

The composition of the gray powder explains perfectly the custom described by Father Ly, of adding 12 parts of white lead to 16 parts of the compound which he calls *pou-pé*.

Ya-pé, or ivory-white, literally tooth-white.—The collection of Chinese colours brought by M. Itier contains a specimen of white completely prepared for painting. The authors have analysed this white. It contains the same constituents as the preceding, except that the alkali is in part replaced by oxide of lead. The composition of this colour, which effervesces a little with nitric acid, is as follows:—

Water and carbonic acid	0·40
Silica	36·00
Oxide of lead	54·00
Arsenic acid	5·60
Oxide of iron	0·80
Lime and magnesia	1·20
Potash and soda	2·00

Arsenic acid appears therefore to be a most important agent in rendering the Chinese colours opake. It would however be a mistake to suppose that the use and properties of oxide of tin are unknown to these people. The authors think that several of the

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numerous whites, forming part of the collection formed by Mr. Rutherford Alcock, owe their great opacity to tin. They have found the following composition for the white enamel of a vase of Chinese manufacture:—

Silica	38·00
Oxide of lead	51·00
Oxide of copper	traces
Oxide of tin	10·41
Potash and loss	0·59

The collection of colours recently sent from China to the Musée Céramique by Mr. Rutherford Alcock contains several specimens of the above-described whites. One of these, it is said, requires an addition of $8\frac{1}{6}$ oz., another of $4\frac{1}{2}$, and a third of $2\frac{1}{2}$ oz. of *yuen-feng* to $1\frac{1}{3}$ lb. of colour. These various additions correspond with the different fusibilities of the primitive colour.

[To be continued.]

PROCEEDINGS OF SOCIETIES.

Royal Society.

June 10, 1852.

(The Earl of Rosse, President, in the Chair.)

"On Rubian and its Products of Decomposition. Part II. Action of Alkalies and Alkaline Earths on Rubian." By Edward Schunck, Esq., F.R.S.

From the author's experiments it appears that rubian is decomposed by the fixed alkalies, and by lime and baryta, but not by ammonia. The products of decomposition formed by the action of the alkalies and alkaline earths are five in number. They are as follows:—1st, *Alizarine*; 2nd, *Verantine*; 3rd, *Rubiretine*; 4th, *Sugar*; and 5th, a new substance, which the author denominates *Rubiadine*. The first four possess the same properties and composition as when formed by the action of acids on rubian. The fifth substance, rubiadine, occupies the place of rubianine, which it closely resembles. It crystallizes from an alcoholic solution in small yellow or orange-coloured needles. It is insoluble in boiling water, and when carefully heated it may be almost entirely volatilized, forming a sublimate of yellow micaceous scales, endowed with considerable lustre. By these two properties it may be distinguished from rubianine, which is soluble in boiling water, and cannot be heated without being decomposed. Its other properties coincide almost entirely with those of rubianine. Its composition is expressed by the formula $C_{32}H_{12}O_8$, and presuming that the formula for rubianine be $C_{32}H_{19}O_{15}$, it would differ from the latter only by the elements of 7 equivs. of water. Besides these substances, there is also formed a small quantity of a dark brown powder, which is soluble in alkalies, but insoluble in water and alcohol. This substance has precisely the same compo-

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sition as the ulmic acid of Mulder, formed by the action of strong acids on cane-sugar. Its formation is doubtless due to the further action of the alkali on the sugar formed in the first instance.

Action of Ferments on Rubian.—It has long been suspected by chemists, that the colouring matter of madder owes its formation to some process of fermentation, but the exact nature of the process has hitherto remained unknown. That some process of decomposition takes place on extracting madder with cold tepid water and exposing the extract to a moderate temperature, is proved by the fact that the extract, if concentrated, becomes after some time thick and gelatinous; and that the process of decomposition takes effect chiefly on the rubian is apparent, since the extract, after it has become gelatinous, is found to have lost its bitter taste and the greater part of its yellow colour.

In order to prepare the peculiar fermentative substance of madder, which has the power of effecting the decomposition of rubian, it is merely necessary to add to an extract of madder made with cold or tepid water, about an equal volume of alcohol. This causes the separation of a quantity of dark reddish-brown flocks, which are collected on a filter and washed with cold alcohol, until the percolating liquid, which is at first strongly coloured, becomes almost colourless. The substance on the filter has the appearance of a dark reddish-brown granular mass, which possesses in an eminent degree the power of decomposing rubian. It is a true ferment, to which the author gives the name of *Erythrozym*. If a quantity of it be added to a solution of rubian, and the mixture be left to stand at the ordinary temperature, a complete change is found to have taken place in the course of a few hours. The liquid is converted into a trembling jelly of a light brown colour, which is perfectly tasteless, insoluble in cold water, and so consistent, that if the solution of rubian was tolerably concentrated, the vessel may be turned over without its falling out. During this process none of the usual signs of fermentation are manifested. The liquid remains perfectly neutral, and no gas of any kind is disengaged. On treating the gelatinous mass resulting from the process with cold water, an almost colourless liquid is obtained, which contains the same species of sugar as that formed by the action of acids or alkalies on rubian. The mass left undissolved by the cold water consists partly of the ferment employed and partly of the substances formed by the decomposition of the rubian. These substances are six in number, of which three are bodies previously described, and three are new. They are,—1st, *Alizarine*; 2nd, *Verantine*; 3rd, *Rubiretine*; 4th, a substance closely resembling rubiacine, which the author calls *Rubiafine*; 5th, a substance very similar to rubianine and rubiadine, on which he bestows the name of *Rubiapine*; and 6th, a peculiar fatty substance which he denominates *Rubiadipine*.

The three latter bodies, which are products peculiar to this process of decomposition, have the following properties:—

Rubiafine is obtained by crystallization from alcohol in yellow glittering plates and needles, which are sometimes arranged in star-

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shaped or plume-shaped masses. It cannot be distinguished by any of its properties from rubiacine; its composition is however different. Like the latter it is converted by the action of persalts of iron into rubiacic acid. The author has again submitted rubiacine and rubiacic acid, together with some of their compounds, to analysis, and from a comparison of their composition with that of rubiafine, he infers that the formula of the latter is $C_{32} H_{13} O_9$, that of rubiacine $C_{32} H_{11} O_{10}$, that of rubiacic acid $C_{32} H_9 O_{17}$; and he inclines to the belief, that by the action of persalts of iron rubiafine first passes into rubiacine, before being converted into rubiacic acid; while by the action of reducing agents rubiacic acid is reconverted; first into rubiacine, and then into rubiafine.

Rubiagine is never obtained in well-defined crystals. When its alcoholic solution is evaporated spontaneously, it is left behind in the shape of small lemon-yellow spherical grains, which when crushed and examined under a lens, are found to consist of small crystalline needles grouped round a centre. When heated it melts, and is decomposed without being volatilized. It is quite insoluble in boiling water. It is soluble in boiling nitric acid, with a yellow colour, and crystallizes out again on the solution cooling in shining needles. Its alkaline solutions are blood-red. The alcoholic solution gives on the addition of acetate of lead at first no precipitate, but the colour of the solution becomes dark yellow, and after some time, provided the solution be not too dilute, an orange-coloured granular precipitate subsides, which is the lead compound of rubiagine. If no deposit is formed, then the addition of water causes an orange-coloured flocculent precipitate, which after being washed with water, in order to remove the excess of acetate of lead, is found to be very little soluble in boiling alcohol, but is easily soluble in a boiling alcoholic solution of acetate of lead with a dark yellow or orange-colour. When rubiagine is treated with a boiling solution of perchloride of iron, it dissolves slightly, but is not converted into rubiacic acid. Rubiagine is distinguished from rubianine by its insolubility in water; from rubiadine, for which it might most easily be mistaken, by its being incapable of sublimation; and from rubiafine by its not being convertible into rubiacic acid. Its behaviour towards acetate of lead, which is different from that of all the other three substances, also serves to characterize it. The most probable formula for rubiagine is $C_{32} H_{14} O_{10}$, from which it appears that it differs from the substances just named merely by the elements of water. Its formation from rubian, like that of the substances allied to it, indicates the simultaneous formation of sugar.

Rubiadipine is a body of a fatty nature, as its name indicates. In its appearance and general properties it resembles rubiretine. It differs from the latter in always remaining soft and viscid, and never becoming hard and brittle, however long it may be heated. Its colour is yellowish-brown. When heated in a tube it emits acrid fumes, similar to those produced by fat when exposed to destructive distillation. When thrown into boiling water it melts and forms oily drops, which rise to the surface. Its alcoholic solution gives with

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acetate of lead a pale reddish-brown precipitate, soluble in an excess of the precipitant. An analysis of the lead compound conducted to the formula $C_{30}H_{24}O_5+PbO$. If this formula be accepted as the true one, the author confesses his inability to explain the formation of rubiadipine from rubian. The great excess of hydrogen contained in it shows that some substance must be formed simultaneously containing a large proportion of oxygen, which has hitherto escaped detection.

Having examined generally the action of erythrozym on rubian, the author next proposed to himself to inquire, by what means this action is either destroyed, retarded, or promoted, and whether any means exist of so modifying the action as to lead to the formation of particular substances in preference to others. From a variety of experiments undertaken with this object, he draws the following conclusions:—

1. There exist no means short of the complete destruction of the ferment, capable of arresting its action on rubian, except exposing it while in a moist state to the temperature of boiling water. Even when exposed to that temperature, after having been previously dried, its fermenting power is not entirely lost, but merely weakened.

2. By the addition of various substances, usually classed as antiseptic, such as sulphuric acid, arsenious acid, sugar of lead, corrosive sublimate, alcohol, and oil of turpentine, during the process of fermentation, the action of the ferment is not destroyed; it is merely retarded and modified.

3. The more the action of the ferment on rubian is retarded, the more rubiretine and verantine, and the less alizarine are formed; so much so, that in some cases the alizarine disappears entirely from among the products of decomposition, which then consist almost solely of rubiretine and verantine. The formation of rubiafine and rubiagine is promoted when the action of the ferment is moderately retarded, but diminishes again or entirely ceases when the retardation is very great. Of the two the rubiagine is the first to disappear when any retardation takes place.

4. By the addition of small quantities of alkalies during the process of fermentation, the action is, as regards its duration, if not promoted, at all events not retarded; and as regards the relative quantities of the various substances produced, the amount of alizarine is thereby decidedly increased, while that of the rubiretine and verantine is diminished.

Most of the ordinary fermentative substances, such as albumen, caseine, gelatine, and yeast, are incapable of effecting the decomposition of rubian, even when mixtures of these various substances with watery solutions of rubian are allowed to stand until they enter into a state of putrefaction. Emulsine is the only substance capable of forming an effective substitute for erythrozym. Its action is similar to that of the latter substance; it gives rise however to the formation of a much larger proportional quantity of alizarine. The action of the peculiar albuminous substance, discovered by Braconnot

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in the root of the *Helianthus tuberosus*, on rubian, was also examined. It exerts only a slight effect on the latter, the only products of decomposition formed being rubiretine and verantine.

The author considers the fact of erythrozym being almost the only ferment which is capable of effecting in any considerable degree the decomposition of rubian, as the best proof of its being a peculiar and distinct substance. When prepared by precipitation with alcohol, erythrozym is obtained as a chocolate-coloured granular mass. When dried it coheres into hard lumps, which are almost black, and with difficulty reduced to powder. When the dry substance is heated on platinum foil, it emits a smell somewhere between that of burning peat and burning horn, and then burns without much flame, leaving a considerable quantity of residue, which on being farther heated is soon converted into a white or grey ash.

After having once been precipitated from its watery solution, even by alcohol, erythrozym cannot again be dissolved in water. If it be mixed while in a moist state with water, it forms a reddish-brown turbid liquid, in which it exists however merely in a state of suspension. Erythrozym is not an uncombined substance, but is a definite compound of an organic body with lime. When treated with acids the lime is removed, and the colour of the substance changes from reddish-brown to yellowish-brown. If a mixture of erythrozym and water be allowed to stand for some time, the former enters into a state of putrefaction, accompanied by a disengagement of gas. After it has entered on this stage of decomposition, it loses in great part the power of decomposing rubian, but acquires that of producing an acid reaction in a solution of sugar. Erythrozym contains nitrogen, but in much smaller proportion than most other fermentative substances. Its composition, when in a freshly precipitated state, is expressed by the formula $C_{56}H_{34}N_2O_{40}+4CaO$. When allowed to decompose, it loses carbonic acid, water, and lime. A quantity which had been employed for the purpose of effecting the decomposition of rubian, and then separated again from the products of the action, had a composition corresponding to the formula $C_{52}H_{32}N_2O_{30}+3CaO$.

In conclusion, the author gives the results of some experiments undertaken with the view of ascertaining whether madder contains more than one colouring matter or not. He infers from his experiments, that the purpurine of other chemists is not a substance of determinate composition; that it consists sometimes of alizarine alone, sometimes of verantine alone, sometimes of a variable mixture of both; that only one colouring matter, viz. alizarine, can be obtained from madder; that purpurine, madder-purple, and the various similar bodies derived from madder, owe their property as colouring matters to an admixture of alizarine; and that they are simply the latter substance in a state of impurity.

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THE CHEMICAL GAZETTE.

No. CCXLIII.—December 1, 1852.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of Essential Oil of Mustard upon Organic Bases. By N. Zinin.

Ammonia, as is well known, enters into combination with oil of mustard. From this circumstance, and also on account of the analogy between the composition of the organic bases and ammonia, the author has treated several of these with oil of mustard. In this manner compounds are obtained which are generally neutral; none of those hitherto procured by the author were of a basic nature.

Naphthalidine and Oil of Mustard, $C^{28}H^{14}N^{2}S^{2}$, or $C^{20}H^{9}N + C^{8}H^{5}NS^{2}$.—If oil of mustard be poured into an alcoholic solution of naphthalidine, it will be perceived, after some time, that a formation of small, white, flat, acicular crystals has taken place on the surface and at the bottom of the mixture; these are united so as to form hemispheres, of which the crystals form radii, and they soon form a strong crust in the fluid. If about 8 parts of alcohol (spec. grav. 0·833) be employed with 1 part of naphthalidine, the greater portion of the compound will be separated in this crust. From 48 parts of naphthalidine and 30 parts of oil of mustard, 51 parts of the compound were obtained by the first crystallization. On evaporating the remaining fluid to the half of its volume, 18 parts were procured in addition.

This compound is insoluble in water; strong alcohol dissolves a small quantity when cold, but a larger quantity when boiling; in æther it is soluble with difficulty; when heated to 266° F., it melts into a clear colourless fluid, which on cooling congeals into a white, granular, crystalline mass. By careful distillation, a considerable portion of the substance is driven over without observable decomposition, in the form of an oleaginous, colourless, or slightly yellow fluid, which on cooling only becomes congealed after long standing, from the formation of granular crystals. By treatment with hydrated oxide of lead, this substance loses its sulphur. The new product thus obtained is readily soluble in alcohol; from the hot alcoholic solution, a white substance, of a silky lustre, crystallizes in a finely granular form; from the remaining solution, water separates a small quantity of a soft unctuous substance, mixed however with the granular crystals, but much more readily soluble than these in alcohol. This compound does not appear to unite with acids; it crystallizes

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without change from alcoholic solutions containing muriatic and sulphuric acids; in a hot, concentrated solution of muriatic acid, it does not dissolve to any greater extent than in pure water. In nitric acid (spec. grav. 1·36), when carefully heated, it forms a colourless solution, in which however reaction soon commences, with violent evolution of red fumes; by this the fluid is rendered yellow, and on the addition of water, a yellow resinous substance is separated from it. But if the acid solution be boiled until the cessation of the red fumes, the addition of water produces an orange-yellow powder, which is readily soluble in alcohol and nitric acid, and less so in boiling water, and which, when heated on platinum foil, fuses into a brownish-red fluid, burns with a slight explosion, and leaves much carbon. Analysis gave—

Carbon	69·72	69·60
Hydrogen	6·00	5·90
Nitrogen.....		
Sulphur	12·98	13·02

Aniline and Oil of Mustard, $C^{20}H^{12}N^2S^2 = C^{12}H^7N + C^8H^5NS^2$. —If to a solution of 1 part of aniline in about 4 parts of alcohol of spec. grav. 0·833, a quantity of essential oil of mustard about equivalent to the aniline be added, combination immediately results, the fluid becomes considerably warmed, the odour of the oil becomes scarcely perceptible, and during cooling a mass of fine foliaceous crystals is formed. If a less concentrated solution of aniline be employed, however, the crystals, which consist of four- and six-sided plates, become 4 millims. long and ½ a millim. thick. They are completely tasteless, inodorous, colourless and transparent, insoluble in water, but readily soluble even in cold alcohol and æther; at 203° F. they melt into a transparent colourless fluid, which congeals on cooling into a radiated crystalline mass. If the temperature be increased until the fluid boils, an odour remarkably similar to that of the leek is evolved, and the fluid afterwards, on cooling, remains long in a sticky state without solidifying; on distillation it furnishes an oily fluid of the same leek-like odour, which, however, cannot be brought to congeal by any means. The sulphur is extracted from the compound of aniline and oil of mustard by the action of hydrated oxide of lead; a compound, very readily soluble in alcohol, is thus produced, so that the alcoholic fluid poured off the sulphuret of lead, after the addition of water until a distinct turbidity remains even when boiling, furnishes, on cooling, long acicular crystals of a silky lustre. These crystals are also slightly soluble in boiling water, and separate therefrom on cooling. From the fluid poured away from the acicular crystals, water throws down a small quantity of a tough, resinous, uncrystallizable substance, which is readily soluble in alcohol, but almost insoluble in water.

The compound of aniline and oil of mustard also appears not to unite with acids; it readily dissolves however with heat in a concentrated solution of muriatic acid, but is separated unchanged from this solution by the addition of water. It is not touched by cold nitric

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acid of spec. grav. 1·36; by careful application of heat, it is dissolved therein, but after a short time a violent action, with evolution of red fumes, takes place; the fluid becomes yellow, and gives a yellow resinous precipitate on the addition of water. The analyses gave—

Carbon	62·80	62·83
Hydrogen	6·50	6·42
Nitrogen		
Sulphur	16·02	16·30

The author has hitherto obtained no compounds by the addition of oil of mustard to alcoholic solutions of the ureas, and of the non-volatile organic alkaloids, such as quinine, cinchonine, morphine and narcotine, even when heated; sulphuret of carbon also appears not to act upon these bases.—*Bull. de St. Pétersb. Phys. Math.*, Cl. x. p. 346.

On the Fat of the Elephant. By MM. FILHOL *and* JOLY.

This substance is white or yellowish, soft to the touch, and nearly inodorous when fresh. Its consistence is like that of lard; it is distinctly neutral with litmus-paper. It melts at 82° F. When deprived of its fluid portion, it is fusible at 118° F. Purified by repeated crystallization from alcohol, its melting-point reaches 122° F.

Whilst it still contains its oleine, it is scarcely soluble in alcohol; but when deprived of this, it dissolves a little better in that liquid. After this operation it becomes very soluble in æther, and is deposited from its solutions in the form of small, brilliant, silky scales, of a dazzling whiteness. 100 parts of the fat of the elephant gave of—

Solid fat (margarine)	21·30
Oleine	78·70

After saponification, we extracted the acids by means of boiling distilled water and hydrochloric acid; we then subjected the mass thus obtained to repeated strong pressure between filtering-paper in order to separate the oleine. The solid portion remaining in the paper was of a dazzling whiteness, soft to the touch, pearly, friable, and entirely soluble in alcohol and æther; it distinctly reddened litmus. Purified by repeated crystallization from alcohol, it was fusible at 139° F.

The solid portion of elephant's fat, and the acid furnished by it, melt precisely at the points indicated by M. Chevreul for margarine and margaric acid.

The elementary analysis also leads us to regard the acid which we have obtained as margaric acid. In fact, we have found it to consist of—

Carbon	75·30
Hydrogen	12·35
Oxygen	12·35

The oleine is of a yellowish colour. Its consistence is similar to that of olive-oil. It is very slightly soluble in alcohol, but dissolves

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in æther with facility. Hyponitrous acid does not transform it into elaidic acid, in which it resembles the drying oils; it does not, however, dry up like these, when exposed to the air.—*Comptes Rendus*, Sept. 20, 1852, p. 393.

On the Mercurial Compounds of the Alkaloids.

By Dr. HINTERBERGER.

[Concluded from page 424.]

On Opianine and its Compounds.—This alkaloid occurs in Egyptian opium. This kind of opium is dry, and contains, as Berthemot has already stated, less morphine than the other kinds of commercial opium. Berthemot states that this sort of opium is more mixed with narcotine and much more difficult to purify. Merck has shown that there is little morphine, but a large quantity of meconic acid in Egyptian opium. By the extraction of Egyptian opium with water, Pereira obtained a gelatinous solution, which could not be rendered clear by filtration.

Engler of Vienna, some years since, worked a large quantity of Egyptian opium for morphine, by extracting the opium with water and adding ammonia to the resulting solution. The precipitate obtained was washed with water, afterwards with alcohol, and then dried. By dissolving this in alcohol, and decolorizing it by means of animal charcoal, he obtained crystals of morphine, which however were intermixed with a quantity of crystals which looked like narcotine. By repeated crystallizations from alcohol, the morphine at last remained in the solution, whilst the narcotine-like crystals were thrown down. The author shows now that the alkaloid taken for narcotine by Engler is a new base, and names it *opianine*, on account of its external resemblance to narcotine, which was formerly called opian.

Opianine, $C^{66}H^{36}N^{2}O^{21}$, crystallizes in long, colourless, transparent, diamond-like needles, which belong to the prismatic system. On being precipitated by ammonia from the muriate, it appears as a white soft powder. It is inodorous; its alcoholic solution has a strong, persistent, bitter taste; and it continues unchanged both at ordinary temperatures and at the temperature of the water-bath. It is insoluble in water, dissolves only in a large quantity of boiling alcohol, and on cooling crystallizes completely from it. Its alcoholic solution has a strong alkaline reaction; it, as well as its salts, is thrown down from this solution by both fixed and volatile alkalies. Opianine forms crystalline double compounds both with chloride of platinum and corrosive sublimate. It is not changed by concentrated sulphuric acid, but dissolves in nitric acid with a yellow colour. Its solution in sulphuric acid to which nitric acid has been added is blood-red, but becomes light yellow after a short time. The analysis of opianine, dried at 212°, gave—

Carbon	62·99	..	..	66	= 396	63·06
Hydrogen	5·698	..	..	36	36	5·73
Nitrogen	..	4·12	4·411	2	28	4·45
Oxygen	..	..	..	21	168	27·76

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In the preliminary notice of this new alkaloid, the author gave the formula $C^{66}\ H^{36}\ NO^{23}$.

Hydrargyro-chloride of Opianine, $C^{66}\ H^{36}\ N^{2}\ O^{21}$, HgCl, HCl.—If an aqueous solution of perchloride of mercury be added to an alcoholic solution of muriate of opianine, a bulky white precipitate results. If this, after being washed with water and dried, be dissolved in a mixture of 2 vols. of alcohol with 1 vol. of concentrated muriatic acid, and water be added to this solution in small quantity, a turbidity will be produced by each addition of water, which however disappears on stirring. By careful addition of water in drops, a turbidity is at length produced, which can no longer be got rid of by stirring the liquid, but which disappears immediately on its being slightly warmed. After about twenty-four hours, concentric groups of acicular crystals are formed in the clear liquid, and these constantly increase. As they are difficult of solution in water and alcohol, they can be sufficiently washed with these substances. The analysis of the substance, dried at 212°, gave—

Carbon.....	49·14	..	66 =	396	49·500
Hydrogen	4·608	..	37	37	4·625
Nitrogen	..	..	2	28	3·500
Oxygen	..	..	21	168	21·000
Mercury	12·28	..	1	100	12·500
Chlorine	..	9·319	2	71	8·875

The muriate of opianine also forms a double compound with chloride of platinum, which is decomposed by an excess of the latter substance, furnishing products, with the study of which the author is still occupied.

Operation of Opianine.—Opianine is a narcotic, which, as far as has yet been ascertained, resembles morphine in its effects. In the comparative investigation of the modes of operation of the two substances, two cats of equal size, six months old, were employed. 0·145 grm. of pure morphine was given to one of these, and a similar quantity of opianine to the other; the same effects were produced in both cases. In eight minutes the pupil in both was so enlarged, that scarcely anything was to be seen of the iris; the pupil was grass-green, and shone brightly; the eyes were motionless. At first they walked about without any fixed object, with the tail drawn in, and with foam hanging from the mouth; their steps afterwards became uncertain, they began to tremble, vomited, dragged their hind legs after them, began to cry out pitifully, and laid themselves down on their bellies, which were much swelled, and generally on their left side. They paid no attention to their names, although at other times they would come immediately on being called, were insensible to ammonia held to them, and took no part in the gambols of the other young cats, which were jumping about them. At the end of an hour the cat to which the morphine had been given had somewhat recovered itself, and ran quickly away when one attempted to touch its belly, which was much swelled. At the expiration of a day, during which they had taken no nourishment, they both recovered.

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On the Elementary Analysis of the Mercurial Compounds of the Alkaloids, and the Method of determining the Mercury.—Hitherto but few of the compounds of organic substances with perchloride of mercury have been investigated; it must not therefore be wondered at that only two methods are known for ascertaining by a single analysis the quantity of mercury, carbon, and hydrogen contained in a given substance.

Nicholson makes, at the anterior end of the combustion-tube, two constrictions, at a distance of an inch from one another, by drawing out the tube when heated. During combustion, the mercury distils over into the space between these two constrictions, accompanied however by a little water. At the conclusion of the combustion, he breaks the tube at the hinder constriction, and separates the water from the mercury by uniting the chloride of calcium tube with an aspirator, and drawing air, dried by means of chloride of calcium tubes, over the mercury heated to 212°, until the chloride of calcium tube no longer shows any increase in weight.

Bunsen's method is less troublesome. The author has employed this method in more than fifty analyses. For such an analysis it is necessary to have—

1. The dry substance. The quantity required for an analysis is between 0·6–1·2 grm. The larger the quantity employed, the more correct will the analysis be.
2. Dry tube for weighing the substance.
3. A dried combustion-tube, of middling width, 26 inches long, and drawn out as usual at one end into a point.
4. A Liebig's potash-apparatus.
5. A tube of the form of a chloride of calcium tube, filled with fragments of potash-lime, and attached to the bulb-apparatus. This potash-lime tube, on an average of forty analyses, intercepted about 0·004 grm.
6. A common tube, filled with solid quick-lime, attached to the potash-lime tube, to protect this from the carbonic acid and water of the air.
7. A common chloride of calcium tube.
8. Cylinders of copper wire. Thick cylinders, 2 inches long and of the size of the combustion-tube, are to be made by twisting together fine copper wire; they are to be heated over the Berzelius lamp until they become black, and then reduced in a stream of dry hydrogen gas. These are preferable to scraps of copper, as they are more easily introduced into the tube.
9. Combustion-furnace. It is to be 30 inches long, made of thin sheet iron; and besides the lower draught pit, is to be furnished with some openings in the iron wall of one end.
10. Chromate of lead, and the other requisites for every elementary analysis.

Mode of performing the Analysis.—a. The weight of the potash apparatus, of the potash-lime tube, of the chloride of calcium tube, and of the tube with the substance under examination, is to be determined; the latter is to be placed again in the steam-bath, and all

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the apparatus again weighed, as well as the substance cooled in the sulphuric acid bath; and in order to make the weighing quickly and with certainty, the weight previously ascertained should be laid in one scale and then the apparatus in the other.

b. The combustion-tube is somewhat more than two-thirds filled with a mixture of the substance and pure well-washed chromate of lead, and upon this two or three of the copper wire cylinders dried in the water-bath are introduced, so that only $2\frac{1}{2}$ inches of the tube remain empty.

c. After emptying the point by a gentle tap or two, and leaving a free space for the escape of the gases, the portion of the tube left empty is to be well wiped out by means of a piece of filtering-paper twisted on a glass rod, by which the small splinters of copper are generally got rid of with difficulty; the combustion-tube is then to be closed with the chloride of calcium tube, and placed in the combustion-furnace.

The end of the chloride of calcium tube inserted into the combustion-tube must not project beyond the cork; otherwise, on the removal of the cork at the end of the combustion, a loss of mercury is thereby produced.

The chloride of calcium tube is connected with the bulb-apparatus, this with the potash-lime tube and the potash-tube; a screen of pasteboard is inserted between the chloride of calcium tube and the potash-apparatus, partly to prevent the heating of the solution of potash, and partly to hinder the sinking of the chloride of calcium tube. The portion of the combustion-tube projecting from the combustion-furnace serves to collect the globules of mercury, and is something more than 2 inches long.

d. When it has been ascertained in the usual manner that the apparatus is air-tight, and the potash-apparatus has been placed in an oblique position, the tube is heated rapidly until the substance is reached, especially covering that part of the tube which is occupied by the copper cylinders with red-hot coals. Arrived at the substance, the combustion is carried on in the same manner as in ordinary organic analysis. When it has proceeded to about the half of the mixture of the substance and chromate of lead, a second screen is to be placed at about an inch from the point of the combustion-tube, and the point, together with the extreme end of the combustion-tube, is to be heated, in order to prevent the backward distillation of the mercury, and to drive out any mercury already deposited in the produced portion. This done, the combustion is continued, the portion of the tube containing the copper being kept at a proper temperature in order to prevent the deposition of water in the space immediately behind the cork. When the operation is well conducted, the mercury is deposited very regularly, and at a distance of about two-thirds of an inch from the screen, in numerous circles of rather large globules; after these come circles of smaller globules, and the smallest globules are situated about one-third of an inch from the cork. This portion of the tube between the cork and the circles of smallest globules of mercury is that on which the

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water deposits itself; this cannot be prevented if too long a piece of the combustion-tube is allowed to project from the furnace.

After breaking off the point, sucking air through the apparatus, and disconnecting the apparatus, the combustion-tube is to be a good deal drawn forth from the furnace without shaking, and laid upon a wooden support covered with a sheet of glazed paper. If the tube cannot be drawn out of the furnace from its being melted to the supports, it is to be broken at the nearest melted place by dropping water on it, and the piece thus obtained to be laid on the wooden support above mentioned. That portion of the tube which was occupied by the cork is now to be held in the hand, whilst at a distance of $\frac{3}{4}$ of an inch from the last circle of the largest globules of mercury a file-cut is made, and the tube is broken with a piece of incandescent charcoal. The piece of tube containing the mercury is carefully removed in a horizontal position to the scales; it is laid upon a quarter of a sheet of glazed paper, and cleaned outside, first with wet and afterwards with dry filtering-paper, and weighed after the lapse of a quarter of an hour. After this weighing, the mercury is very carefully removed from the tube, taking care to break away no part of the sharp edge of the tube; the weight of the empty tube is now to be determined. The difference between the two weights gives the weight of the mercury furnished by the combustion of the substance examined.

The increase of weight of the chloride of calcium tube does not, in most cases, furnish the exact quantity of water, because a small quantity of mercury is always distilled over into the narrow tube of the chloride of calcium tube. On this account the chloride of calcium tube must be allowed to lie stopped for twelve hours in a safe place, then again weighed, the mercury removed from the narrow tube by means of small paper cylinders, and its weight determined. The quantity of mercury so obtained is to be added to that previously procured, but its weight must be deducted from that obtained for the water.—*Sitzungber. der Akad. der Wissensch. zu Wien*, vii. Hft. 3.

On Neutral Molybdate of Ammonia. *By* F. A. Flückiger.

In preparing ordinary molybdate of ammonia by the method recommended by Prof. Delffs*, the author has frequently obtained, after evaporation and the crystallization of the salt, while the mother-liquor smelt strongly of ammonia, a muddy crystalline deposit, which would not dissolve on the addition of water and heating. According to Svanberg and Struve†, this is the acid salt. This is however disproved by the analyses of Prof. Delffs‡, according to which the true molybdate of ammonia ($AmO, 2MO^3 + HO$) is no other than that to which they assign the extraordinary formula $NH^4O, 2MO^3 + NH^4O, 3MO^3 + 3HO$. Flückiger for this reason conjectured that the deposit in question might be a neutral salt. As it did not appear

* Poggendorff's Annalen, lxxxv. 450. † Journ. für Prakt. Chem., vol. xliv.
‡ Poggendorff's Annalen, lxxxv.

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to be homogeneous, he heated the liquid containing the deposit, which he then dissolved by the addition of an enormous excess of concentrated caustic ammonia. After some hours, transparent needles, more than an inch long, crystallized out. When the mother-liquor was further evaporated until the deposit was again formed, another crop of crystals was obtained by dissolving it in ammonia. Sometimes short regular prisms were obtained. The form of the needles could not be determined, owing to their extreme brittleness.

The salt thus obtained became immediately opake upon exposure to the air, owing to the loss of ammonia, with retention of form. When very rapidly dried, the crystals may be obtained transparent and brilliant. Heated in a glass tube, they do not evolve water, or at least more than might result from mechanically-mixed mother-liquor, from which they could not be entirely freed, on account of the easy decomposability. This may also be the reason why accurate results were not obtained in the analysis, which was conducted by igniting the salt in a glass tube, through which a stream of dry hydrogen was passed, reducing it to MO^2:—

1·108	gave	0·695 MO^2	=	62·73 per cent.
0·736	...	0·460	...	62·50 ...
1·024	...	0·638	...	62·30 ...
0·765	...	0·480	...	62·76 ...

This residue ought, according to the formula AmO, MO^3 (M=46), to amount to 64·58 per cent. Still there is no other rational formula conceivable with which the analytical results will correspond better. Even $AmO, MO^3 + HO$ would give 59·05 per cent. MO^2.

Flückiger satisfied himself that his salt agreed in form with that which Svanberg and Struve precipitated from an ammoniacal solution of molybdic acid by alcohol, and had regarded as the anhydrous neutral salt. He considers it possible that the greater accuracy of their analytical results may be owing to their having crystallized the salt from alcohol.

The formation of this salt evidently depends upon the previous formation of the acid salt, the water of which is replaced by ammonia. It is interesting that in one case absolute alcohol is the dehydrating agent, while in the other it is ammonia which performs this office. The neutral salt is more soluble than the acid salt, but a solution of the former naturally yields on evaporation only the acid salt.

The general close resemblance between tungsten and molybdenum, especially in their tendency under certain circumstances to form acid salts with ammonia, induced Flückiger to attempt the formation of a neutral tungstate of ammonia in a solid form. In this he was unable to succeed.—Poggendorff's *Annalen*, lxxxvi. 594.

On the Adulteration of Sulphate of Quinine. *By* D. Zimmer.

At present a great quantity of quinine containing quinidine is met with in commerce. The sulphate of quinidine is much heavier

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and less flaky than sulphate of quinine. The sulphate of quinidine is far more soluble in water and absolute alcohol than the other salt; when exposed to the air, it loses its water of crystallization, without acquiring an effloresced appearance, remaining crystalline. As a distinction between quinine, cinchonine and quinidine, the author states that a mixture of 60 drops of æther and 20 drops of solution of ammonia dissolves at least 10 grs. of pure sulphate of quinine, but only 1 gr. of sulphate of quinidine. If therefore sulphate of quinine, containing cinchonine and quinidine, be thus tested, the two latter will remain if there be more than 1 gr. of sulphate of quinidine in 10 grs. of the salt. Even this small quantity may be ascertained if the æther be previously saturated with quinidine. Quinidine is distinguished by crystallizing from the ætherial solution after a certain time; it may be distinguished from cinchonine by its being dissolved on the addition of a larger quantity of æther, the cinchonine remaining undissolved.—Buchner's *Repert.*, i. p. 143.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Composition of the Substances employed by the Chinese in the Decoration of Porcelain. By MM. Ebelmen *and* Salvétat.

[Continued from page 436.]

2. *Blacks.*

The authors have analysed four different specimens of blacks, namely, the black called *Si-fen-liao*, in the collection of the Musée Céramique, and the shining, dull, and bright blacks of the collection brought from Canton by M. Itier. The results are as follows:—

	Fen-liao. I.	Ou-kin. II.	Liang-he. III.	Tse-he. IV.
Loss by heat	14·20	25·60	3·20	16·60
Silica	2·00	1·98	50·70	6·00
Oxide of lead	69·14	59·58	25·00	traces
Oxide of copper	4·60	8·40	5·80	5·40
Oxide of iron	3·00			
Oxide of manganese	7·00	1·70	10·02	70·00
Oxide of cobalt				
Alumina	0·24	0·62	0·52	0·40
Lime and magnesia	0·60	1·43	1·67	1·20
Alkali	0·00	0·69	3·09	0·40

I. *Si-fen-liao.*—This is a brown powder with a greenish tinge. It effervesces strongly when treated with dilute nitric acid, and the solution presents all the characters of nitrate of lead. Before the blowpipe and with reagents it behaves like a mixture of white lead and an oxide of manganese containing cobalt.

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II. *Ou-kin*, metallic black or raven-black (ticketed *noir mat*).—This is in elongated fragments of the form of small sticks, or in irregularly rounded masses.

With reagents it behaves like *si-fen-liao*. It differs from that colour in being made up into masses with size; but when this is removed, both colours consist of 5 parts of white lead and 1 part of the mineral called *thsing-hoa-liao*. It follows also from the analyses that this mineral must be of very variable composition.

In both these blacks the silica is only introduced by the gangue of the manganesian mineral, and this circumstance occurs also in other colours. It explains certain effects which may be remarked in the decoration of some Chinese porcelain, which are adorned with dull black or red ornaments, forming an agreeable contrast with the other well-glazed ornaments.

Laid on porcelain and exposed to the heat of the muffle-furnace, the two preceding colours only adhered in the thin parts. Where they were thicker, the oxide of lead was absorbed by the oxides, which in the absence of silica were incapable of forming a vitreous varnish. The thin portions, on the contrary, shone, because in these parts the small quantity of silica was sufficient to transform the oxide into silicate of lead.

III. *Liang-he*, shining black (ticketed *noir luisant*).—This is a brown powder, which must have been formed from a previously fused mass. With nitric acid it effervesced slightly, and the solution contained lead. Before the blowpipe it gave the reaction of cobalt. Oxide of manganese exists in it in smaller quantity than in the preceding colours.

IV. *Tse-he*, porcelain-black (ticketed *noir clair*).—This consists of dark greenish fragments, which are crushed with difficulty, and when burnt emit a distinct odour of burnt glue. It appears to be a mixture of *thsing-hoa-liao* with a size formed from bullocks' hides (*yeou-p'hy-kao*), which, according to Father Ly, is the solvent employed by the Chinese to render their colours fit for use. The silica, which forms 6 per cent. of the mass, is much contaminated with alumina; it is the gangue of the cobaltiferous mineral. The authors have tried this black as a blue under glazing; it gave blue designs perfectly resembling those which occur on many specimens of Chinese porcelain. As however the temperature of the furnaces at Sèvres is greater than that of the Chinese furnaces, the portions on which the oxides were thickly laid became inflated during the baking.

3. *Blues.*

The collection sent by Father Ly contains four different specimens of blue,—two in the rough state, and two completely prepared for painting. From the analyses it appears, that, in conformity with the statement made by Father Ly, there is no difference between the rough and prepared colours.

Seng-khouang-thsei, or rough blue of the first quality, requiring no addition of *yuen-feng*; it must be pounded (Ly).

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This colour is in well-fused, brilliant, transparent masses, of a fine sky-blue. It is frequently paler and opake in the interior of the masses; this appears to arise from imperfect fusion. When powdered, it is of a paler but pure blue colour; and if treated immediately after this operation with dilute nitric acid, it does not effervesce.

Si-khouang-thsei, or prepared blue of first quality (Ly).—This is a powder which effervesces slightly with nitric acid from the presence of a little carbonate of lead. With acids it behaves like the preceding, resisting their action very well. Muriatic and nitro-muriatic acids discolour it completely after long boiling.

Seng-ting-thsei, rough blue of second quality, without need of *yuen-fang* (Ly).—This consists of perfectly transparent blue fragments. When triturated, it furnishes a powder of a paler and more violet colour than that given by the *khouang-thsei*. With acids it behaves like that colour.

Si-ting-thsei, or prepared blue of second quality (Ly).—This is the powder furnished by pounding the preceding. It effervesces slightly with dilute nitric acid.

The following are the results of our analyses of these four colours:—

	Khouang-thsei.		Ting-thsei.	
	Seng.	Si.	Seng.	Si.
Loss by heat.....	0·00	3·80	0·65	2·40
Silica.....	48·21	46·40	36·81	37·20
Oxide of lead	32·84	30·89	44·14	42·18
Oxide of cobalt	1·50	1·60	0·68	0·50
Oxide of iron	1·63	1·50	1·03	1·06
Lime.....	0·97	0·85	0·83	0·64
Magnesia	trace	trace	trace	trace
Potash and soda	13·78	13·20	11·10	13·39
Oxide of copper	1·00	0·96	0·50	0·15
Oxide of manganese....	0·50	0·62	1·00	1·00
Alumina	0·06	0·15	0·50	0·50

In the second and fourth analyses, the loss includes the water and carbonic acid of the carbonate of lead formed by exposure to the atmosphere. The difference in the proportions of the oxides of cobalt and manganese explains the difference in the tint of these two blues; the second is paler and more violet than the other.

M. Itier brought the two following blues from Canton.

P'ao-lan, precious blue (ticketed *bleu foncé*).—This is a powder containing fragments. It resists the action of acids better than the preceding blues, but effervesces slightly with them. Under water it is seen to consist of two powders of different blues.

Tsing-fen, blue powder (ticketed *bleu de ciel foncé*).—This is a paler powder than the preceding. It effervesces slightly, and resists the action of acids rather less than the *p'ao-lan*.

The analyses of these two colours gave—

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	P'ao-lan.	Tsing-fen.
Loss by heat	3·00	1·40
Silica with traces of stannic acid	60·80	47·20
Oxide of lead	18·76	38·90
Oxide of cobalt	1·62	0·50
Oxide of iron	1·50	1·00
Lime	1·08	0·64
Magnesia	trace	trace
Potash and soda	0·19	9·34
Oxide of copper	1·00	trace
Oxide of manganese	1·50	0·84
Alumina	0·55	0·18

Thus all Chinese blues consist of a plumbo-alkaline glass coloured with oxide of cobalt. The only difference between them lies in their various degrees of fusibility.

4. *Greens.*

All the greens employed in the decoration of porcelain in China are coloured by oxide of copper, sometimes pure, sometimes rendered yellowish by the addition of a prepared yellow, or bluish by the addition of white or of a harder flux.

The authors have only examined the rough colours, as, according to the statements of Father Ly, the prepared colours would only differ from the rough ones in being triturated, or sometimes mixed with white lead.

Fei-thsei, rough green of first quality, to a pound of which 12 oz. of *yuen-feng* are added (Ly).

This is of a turquois-blue colour; its powder is pale sea-green. Father Ly says, that when this colour is of a coarse quality, it is mixed with *sy-chy-mo*. The authors think that it must be in a similar case that the large addition of *yuen-feng* mentioned above is necessary, as this addition does not appear to be required with the specimen in the Musée Céramique.

This colour is produced by the fusion of white with the following green. In M. Itier's collection there are two greens of the same shade,—one which M. Itier calls light blue (*bleu clair*), and another which he names sea-green (*vert d'eau*).

Tcha-lan, light blue (ticketed *bleu clair*).—This is a fine powder of a pale turquois-blue. By immersion in water, two different powders are perceived in it,—one blue, the other white or grayish. The latter lowers the strength of the blue. The mixture effervesces slightly with nitric acid.

Chan-lou, mountain-green (ticketed *vert d'eau*).—This is a homogeneous powder, very similar to the *fei-thsei* of Father Ly's collection. The colour is derived from deutoxide of copper.

The analysis of these three greens gave the following results:—

	Fei-thsei.	Tcha-lan.	Chan-lou.
Loss by heat	0·50	2·40	1·00
Silica with traces of stannic acid	37·50	41·50	42·44
Oxide of lead	44·13	43·40	43·40

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	Fei-thsei.	Tcha-lan.	Chan-lou.
Oxide of copper	3·00	2·40	3·41
Alumina and oxide of iron	trace	0·86	1·26
Lime	0·25	2·11	2·00
Arsenic acid	4·00	7·33	6·49
Potash and soda	10·00		

The presence of an opake white is not necessary for the production of this tint with oxide of copper; the addition of a silico-alkaline flux, containing equal parts of sand and oxide of lead, is sufficient to produce this tint from the *chang-lou* green, which is now to be described. It is therefore possible that there is no white in M. Itier's "pale blue," and that the grayish particles are simply a plumbo-alkaline flux.

Seng-chang-lou, green of the fourth quality, to (a pound of?) which 5 oz. of *yuen-feng* are added (Ly).

This occurs in masses of a sap-green colour; its colouring principle is oxide of copper; it contains no trace of oxide of chromium. Two samples in the collection of the École des Mines have the same appearance. Analysis:—

Moisture	0·67
Silica	41·20
Oxide of lead	49·05
Oxide of copper	5·05
Alumina	0·17
Oxide of iron	0·05
Lime	0·12
Potash	3·96
Soda	0·60

Seng-chang-kou-lou, green of the fifth quality, to a pound of which 5 oz. of *yuen-feng* are to be added (Ly).

The rough colour is a mixture of fused vitreous fragments of two shades. Of these some are green, and resemble the green *seng-chang-lou*; the others yellow, and similar to the *chang-hoang*, which will be presently mentioned. The samples in M. Itier's collection and in that of the École des Mines confirm this view of the composition of this colour. By separating the fragments and weighing them separately, the authors found that the proportions were, of—

Chang-lou (green)	60
Chang-hoang (yellow)	40

The green fragments, analysed separately, gave the same composition as the *chang-lou*:—

Humidity	0·51
Silica	41·50
Oxide of lead	48·40
Oxide of copper	5·50
Alumina	0·40
Oxide of iron	0·07
Lime	0·18
Potash and soda	3·44

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The analysis of the separated yellow fragments gave 40 per cent. of silica; they were coloured with antimony.

Eul-lou, second green (ticketed *vert jaune clair*).—This is a very fine powder, of a pale greenish-yellow colour; on immersion in water, it is seen to consist of a mixture of green and yellow particles. It effervesces slightly with dilute nitric acid, the acid taking up lead.

Fen-lou, green powder (ticketed *vert jaunâtre clair*).—It is an intimate mixture of three different substances (green, yellow and white), which can only be distinguished well by immersing the powder in water. The colour of the mixture is a pale yellowish-green; it effervesces with dilute nitric acid, and the acid afterwards contains lead.

The analysis of these two greens gave the following results:—

	Eul-lou.	Fen-lou.
Loss by heat	2·60	2·50
Silica with traces of stannic acid	33·30	36·80
Oxide of lead	53·14	51·04
Oxide of copper	0·60	0·51
Oxide of antimony	3·00	2·01
Alumina and oxide of iron	1·06	1·12
Lime	2·11	1·74
Magnesia	0·03	0·05
Arsenic acid	..	0·50
Alkalies and loss	4·16	4·23

The authors remark that there is a great uniformity in the composition of the flux in all these green colours; the following differs from them in this respect, but the difference is diminished by the addition of a large quantity of oxide of lead.

Seng-ty-lou, rough green of the sixth quality.—For use it must be pounded and mixed with *yuen-feng*, 19 oz. of the latter to a pound of colour (Ly).

According to the catalogue of the École des Mines, this green is procured from the district *Fou-leang-hien*. It is a very complex substance, formed of fragments of a sap-green colour, like *chang-lou*, and of a granular brownish powder with a tinge of violet. These substances are in the proportion of 75 parts of the green fragments to 25 of the powder. The green fragments present the reactions of the *seng-chang-lou*; like it they contain 41 per cent. of silica.

The brownish powder may be separated into three substances by washing in water:—

1. A green powder, which is certainly the result of the friction of the fragments of *chang-lou*.
2. A grayish sand-like powder, with the properties of *sy-chy-mo*.
3. A violet powder containing copper.

Nitric acid dissolves the brown powder with evolution of nitrous vapours, leaving the gray and green powders untouched. The solution contains copper. Dilute muriatic acid acts in the same manner, but when concentrated it also dissolves a little oxide of lead. Analysis:—

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Silica	67·9
Oxide of lead	2·0
Copper	20·7
Oxide of iron	1·0
Lime	0·3
Alumina	0·5
Oxygen, potash and loss	7·6

The copper is here regarded as metal, as it exists in the substance in two states of oxidation. This composition fully accounts for the large addition of white lead indicated by Father Ly.

When triturated, this colour forms a dull violet-brown powder, but after baking it gives a bright green, similar to that furnished directly by the *chang-lou*.

In M. Itier's collection there is a similar colour, which he calls Scheele's green.

Ta-lou, grass-green (ticketed *vert de Scheele*).—It is a nankeen-coloured powder, united into irregular fragments, and giving a green tint by the action of fire. It effervesces with dilute nitric acid, and the solution contains lead. Nitric acid does not attack it when heated; the nankeen colour remains, which renders it probable that the copper is in the state of protoxide. Muriatic and nitromuriatic acids attack it completely; a mixture of oxide of lead and deutoxide of copper is dissolved. Analysis:—

Loss by heat	4·30
Silica	35·20
Oxide of lead	51·05
Oxide of copper	3·98
Alumina and oxide of copper	1·40
Lime	1·00
Magnesia	traces
Stannic acid	traces
Alkali and loss	3·07

All these greens consist therefore of a glassy flux, in which a few parts of oxide of copper are dissolved. The authors remark also that their direct experiments show that oxide of lead increases the greenness of the tint obtained from the oxide of copper. Soda produces a glass of which the tint is less blue than that obtained with an equal quantity of potash under similar circumstances.

5. *Yellows.*

The Chinese produce yellow on porcelain by means of antimony. There are, in the collections examined by the authors, several yellows, both in the rough and prepared state. They are called *thsing-hoang*, *chang-hoang*, *yan-hoang* and *hoang-se*.

The authors have analysed the rough *chang-hoang* in the collection of Sèvres, and the *hoang-se* brought by M. Itier. The others offered so close a resemblance to these, that it was not thought worth while to analyse them.

Seng-chang-hoang, or yellow, to a pound of which 5 oz. of *yu en-*

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feng are added (Ly).—This is in bright yellow, fused, puffy fragments, with a slight greenish tinge. When reduced to powder, it is attacked by muriatic acid. Analysis:—

Humidity	1·13
Silica	40·47
Oxide of lead	51·53
Oxide of copper	0·35
Alumina and oxide of iron	traces
Lime	0·17
Antimonic acid	3·60
Potash	3·39
Soda	0·71

Hoang-se, yellow (ticketed *jaune*).—This is a pale yellow powder, which appears to be homogeneous even under water; it effervesces very slightly with dilute nitric acid, and the solution contains lead. The analysis shows that it is the same yellow as the *chang-hoang* of Father Ly, with the addition of a small quantity of the *yuen-feng*, which, he states, should be added to that colour to render it fit for use. Analysis:—

Loss by heat	2·10
Silica with traces of oxide of tin	33·00
Oxide of lead	54·14
Oxide of copper	0·30
Antimonic acid	3·27
Alumina and oxide of iron	0·80
Lime	0·70
Magnesia	0·60
Alkalies and loss	5·09

All the Chinese yellows have therefore the same flux. To reproduce them, the following mixture must be slightly melted together:—

Orange minium	8
Sand	4
Antimony	4

This gives a fusible Naples-yellow.

The following mixture is then thoroughly melted into a transparent glass:—

Orange minium	44
Sand	36
Fused carbonate of soda	7

The two substances are then triturated together, and a yellow will be obtained having the same composition and properties as the *chang-hoang*.

[To be continued.]

Note on the Preparation of Liquid Glue. *By* M. S. Dumoulin.

All chemists are aware, that when a solution of glue (gelatine) is heated and cooled several times in contact with the air, it loses the

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property of forming a jelly. M. Gmelin observed, that a solution of isinglass, enclosed in a sealed glass tube and kept in a state of ebullition on the water-bath for several days, presented the same phænomenon, that is to say, the glue remained fluid, and did not form a jelly.

The change thus produced is one of the problems most difficult of solution in organic chemistry. It may be supposed, however, that, in the alteration which the glue undergoes, the oxygen of the air or of the water plays a principal part; what leads me to think this is the effect produced upon glue by a small quantity of nitric acid. It is well known, that by treating gelatine with an excess of this acid, it is converted by heat into malic and oxalic acids, fatty matter, tannin, &c. But it is not thus when this glue is treated with its weight of water and with a small quantity of nitric acid; by this means a glue is obtained which preserves nearly all its primitive qualities, but which has no longer the power of forming a jelly. Upon this process, which I communicated, is founded the Parisian manufacture of the glue which is sold in France under the title of "*colle liquide et inaltérable.*"

This glue being very convenient for cabinet-makers, joiners, pasteboard-workers, toy-makers, and others, as it is applied cold, I think it my duty, in order to increase its manufacture, to publish the process.

It consists in taking 1 kilogrm. of glue, and dissolving it in 1 litre of water in a glazed pot over a gentle fire, or, what is better, in the water-bath, stirring it from time to time. When all the glue is melted, 200 grms. of nitric acid (spec. grav. 1·32) are to be poured in, in small quantities at a time. This addition produces an effervescence, owing to the disengagement of hyponitrous acid. When all the acid is added, the vessel is to be taken from the fire, and left to cool.

I have kept the glue, thus prepared, in an open vessel during more than two years, without its undergoing any change. It is very convenient in chemical operations; I use it with advantage in my laboratory for the preservation of various gases, by covering strips of linen with it.—*Comptes Rendus*, Sept. 27, 1852, p. 444.

On a Green Colouring Matter from China. By J. Persoz.

M. Daniel Kœchlin-Schone forwarded to me, last autumn, a sample of calico dyed in China, of a sea-green tint of great stability, requesting me to examine into the composition of this green colour. All the attempts to ascertain the presence of either a yellow or blue, which I made with this specimen, met with no success; and I was soon convinced, by isolating the colouring matter, that this green was produced by a tinctorial substance *sui generis*. It also became evident—

1. That this colouring matter was of a vegetable origin.

2. That the stuff upon which it was fixed was charged with a large quantity of alumina and with a little oxide of iron and lime, substances the presence of which necessarily implied that the colour-

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ing matter employed had required the assistance of mordants to make it adhere to the stuff.

These results, so positive, and yet so contrary, not only to all we know in Europe with regard to the composition of greens, but also to all that has been written on the processes employed by the Chinese in dyeing this colour, necessitated a closer examination on my part. I therefore had recourse to the assistance of Mr. Forbes, American Consul at Canton, to obtain a specimen of the substance. He had the goodness to send me about 1 grm. of it.

This substance is, in thin plates, of a blue colour, resembling that of Javanese indigo, but of a finer grain, and differing also from indigo in its composition and all its chemical properties. On infusing a very small fragment of it in water, this fluid soon acquired a deep blue colour with a greenish tinge. On gradually bringing the liquid to boil, and immersing in it a piece of calico on which mordants of iron and alumina had been printed, a genuine dyeing took place, the portions of the stuff which were coated with alumina acquiring a sea-green colour of greater or less intensity according to the strength of the mordant, those which were coated with alumina and oxide of iron becoming deep sea-green with an olive tinge, and those charged with pure oxide of iron dark olive. The portions of the calico not coated with mordant remained white.

The colours thus obtained were exposed to all the agents to which the Chinese green had previously been submitted, and behaved in the same manner. From these experiments we may conclude—

1. That the Chinese possess a colouring matter, having the appearance of indigo, which communicates a green colour to mordants of alumina and iron.

2. That this colouring matter neither contains indigo nor any derivative of this dyeing principle.—*Comptes Rendus*, Oct. 16, 1852, p. 558.

On Stannate of Soda.

The stannate of soda occurs now frequently in commerce, and is employed in dyeing, like chloride of tin. It is prepared by boiling a solution of caustic soda, of 15°–20° of strength, with scraps or sheets of tin and litharge or sulphate of lead; the latter substances give their oxygen to the tin, and facilitate the oxidation. The powder of lead separated is reoxidized in the air, and can be again employed.—Buchner's *Repert.*, p. 368.

PATENTS.

Patent granted to C. A. Kurtz, *for the Preparation of Madders and Munjeet.*

This invention consists in preparing madders and munjeet, by combining therewith preparations of liquor which will tend to produce fermentation, as hereafter explained.

The liquor is first made in the following manner:—20 lbs. of crushed malt are boiled in 100 gallons of water from twenty to thirty minutes; after which about 45 lbs. of bran are stirred in, and

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the liquor allowed to stand until the malt and bran fall to the bottom; and then the clear liquor is run off, and the remainder filtered. From 60 to 65 gallons of the liquor are added to 100 gallons of water, which is of such a temperature that the mixture will be about 112° F. This liquor is put into a vessel capable of containing from 260 to 300 gallons, and about 3 cwt. of madder or munjeet are added, and the whole stirred at intervals of from ten to fifteen minutes until it becomes a homogeneous mass; this is to be left to rest till signs of fermentation present themselves, which are to be checked by repeated stirrings during a period of from sixteen to eighteen hours. The mass is then to be filtered, pressed, dried, ground, and packed in the usual way.

The patentee remarks, that, in place of malt and bran, other grain or matters may be employed in preparing a mash or liquor which will tend to produce fermentation in like manner; but he believes that malt and bran are the best for the purpose. He further observes, that, although he has been particular in stating the materials and exact quantities and temperatures according to the best of his knowledge, he does not confine himself thereto, as they may be varied without departing from his invention so long as extraneous matter be employed to induce fermentation.—Sealed April 17, 1852.

Patent granted to Mercer *and* Greenwood, *for preparing Cotton and other Fabrics for Dyeing and Printing.*

This invention relates to the preparation of cotton and other fabrics with oil, which is called, in the art of dyeing Turkey-red, the "oiling process;" and it consists in causing the fabrics to be wet with water, or a watery solution, when passed through or impregnated with oil.

The patentees take cotton, or other fabric, in the ordinary partially bleached state, and wet it with water or a watery solution of carbonate of potash or soda, containing 4 or 5 oz. thereof to the gallon (preferring to use the "padding-machine" for this purpose); and in this wet state they pass it through olive-oil at a heat below that of boiling water—from 140° to 160° F.

The oil is contained in a cistern, having a series of rollers in it, and at one end a pair of padding-bowls. The wet fabric is conducted through the oil, and under and over the rollers, and is then passed between the padding-bowls. The fabric is then taken to the stove, and dried by exposure to a temperature of from 160° to 180° F.; and afterwards it is treated with dilute solutions of carbonated alkalies, and stoved in the usual manner. Instead of the oil being employed at a temperature below that of boiling water, it may be used above the heat of boiling water, and then its temperature is preferred to be from 240° to 300°; in other respects the process is the same as before described. In this case the heat of the oil changes the water in the fabric, while passing through it, into steam, which ascends through the oil and escapes.

The patentees state that they prefer to use olive-oil in which carbonate of potash or soda has been dissolved, in the proportion of 6 or 8 oz. to the gallon.—Sealed March 15, 1852.

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THE CHEMICAL GAZETTE.

No. CCXLIV.—December 15, 1852.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Fat of Potatoes. *By* Dr. H. EICHHORN.

SINCE the true constitution of both vegetable and animal fats was pointed out by the investigations of Chevreul, their accurate study has continually occupied the attention of chemists. A knowledge has thus been obtained of one of the most definite groups of organic chemistry, the fatty acids having the general formula $C^n H^{n-1} O^3 + HO$. The fats which have been examined occur abundantly in vegetables and animals; they may either be obtained in commerce, or easily extracted from organic bodies for the purposes of investigation. The case is different with certain fats existing in many vegetable organs in such small quantity, that at the utmost we are acquainted only with some few of their physical characters and their per-centage quantity. Such, for instance, are the minute quantities of fat present in potatoes, beet, maize, rice, the cereals, lentils, peas, &c. The extraction of this fat is attended with great difficulties; very large quantities of the vegetable substances must be treated with æther or alcohol, in order to obtain enough for examination.

Notwithstanding these difficulties, it appeared to me of interest to examine these fats more closely, because, as all the substances employed in the manufacture of alcohol contain such small quantities of fat, the question naturally suggests itself, whether the fusel oils passing over with the alcohol on the distillation of the fermented liquors may not originate from these fats either as products or educts. Potatoes were chosen for the present investigation, on account of their agricultural and dietetic importance; although it has not furnished the full analytical data requisite for the accurate deduction of the constitution of the fat, this deficiency must be chiefly attributed to the difficulty in obtaining material.

The per-centage of fat in potatoes has been variously estimated. Michaelis* found 0·056; Liebig†, 0·067; Henri‡, 0·1. Boussingault§ estimated the per-centage of fat in the entire tubers at 0·14, and in the peelings at 0·21. The fat from fresh red potatoes was colourless; that from old white potatoes, yellowish-brown, tasteless, with a very pleasant odour and the consistence of butter. Eichhorn

* Journ. f. Prakt. Chem., xiii. p. 189.
† Compt. Rend., 1843, p. 568.
‡ Boussingault's Econ. Rur., p. 254.
§ Ann. Chim. Phys., xiv. p. 423.

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has likewise estimated the per-centage of fat; and in order to obtain it in as normal a state as possible, did not dry the potatoes, but treated the fresh-rasped substance with æther until the latter was no longer coloured. After distilling off the æther, the fat was weighed upon a watch-glass. He found in unpeeled white potatoes 0·082 and 0·065 per cent. of a greenish, soft, aromatic-smelling fat, mean 0·073; in the peel of red potatoes*, which had been stored through the winter in a cellar, 0·384 per cent. of a greenish-brown fat of unpleasant odour, which gives 0·039 per cent. for the entire tubers. According to these data, and assuming the mean per-centage of fat in potatoes to be 0·073, the peelings contain one-half of the fat and five times as large a per-centage as the interior substance.

These results correspond, as far as can be expected, with the data given by Henri, Michaelis and Liebig. Boussingault, however, found twice or three times as much fat. Perhaps this may be owing to the more complete extraction of the fat from the tubers when dry and powdered, as he employed them. It will be evident, from the above estimations, that very large quantities of æther would be requisite to obtain any available amount of fat. Eichhorn therefore adopted the following method, which enabled him to obtain the fat more conveniently, if not so completely.

When the pasty mass obtained by grating potatoes is pressed in a linen cloth, a milky liquor is separated, which under the influence of the atmosphere assumes a violet-red colour upon the surface. The starch soon subsides, leaving the liquid almost translucent. However, on standing it again becomes turbid, and in the course of an hour has a whitish-yellow colour. Eichhorn at first supposed that this change was attributable to the substance which communicates the dark colour to the juice in sliced potatoes. He therefore filtered the recently-expressed juice in an apparatus filled with hydrogen. The filtration proceeded very slowly, in consequence of the firm adhesion of the suspended matter to the filter. The juice did not suffer any alteration while in the atmosphere of hydrogen; but when, after passing through the filter, it came in contact with the air, it assumed the usual violet-red colour. The whitish-yellow residue left upon the filter proved to be a fatty body, soluble in æther, having a pale yellow colour and the consistence of hard butter. This showed that the turbidity of the liquor after the deposition of the starch was owing to the separation of previously-dissolved fat; he was however unable to detect the presence of fat-globules in the turbid liquor, such as are observed in milk.

This separation of fat from potato-juice has long been known to the starch-manufacturers; and they are obliged, on this account, to separate the uppermost layer of the starch-sediment, in order that the whole may not have a dirty appearance. The fat appears to adhere to fine threads of cellulose suspended in the juice, and to be deposited with them, forming the yellowish layer always observed upon the starch-sediment; and it is consequently very probable that

* 935·0 grms. gave 95·0 gr. of peel, from which was extracted 0·365 grm. fat.

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the minute quantity of fat which has been detected in starch may be derived from this source.

When such turbid potato-juice is boiled, the albumen coagulates, and carries the fat to the surface. It may be extracted from the coagulum by small quantities of æther.

Eichhorn made use of peeled potatoes to obtain the fat, because he found they yielded a harder and paler coloured fat than the entire tubers. The juice of 300 lbs. of grated potatoes, passed through a hair-sieve, was allowed to stand for a while, then boiled, the coagulum separated by a linen cloth, and to prevent any possible alteration of the fat while drying, treated moist with boiling æther; the ætherial liquor was then distilled off to about a fourth, from which stellar groups of very delicate needles separated on cooling. They consisted of a wax-like substance, perfectly white, slightly soluble in æther and alcohol, not altered by caustic potash; heated to 518° F. in an oil-bath, it became slightly brown, but did not melt, and it was only by heating it on platinum foil that it became liquid, decomposing at the same time and burning with a bright flame, thus closely corresponding in these respects with cork-wax. Two analyses gave in 100 parts—

	XII.	XIII.		
Carbon	71·36	71·32	36	71·52
Hydrogen	10·10	10·06	30	9·93
Oxygen	18·54	18·62	7	18·55

a composition agreeing best with the formula $C^{36}H^{30}O^{7}$.

By the further evaporation of the original ætherial solution on a water-bath, about ½ an ounce of a second fat was obtained having a yellow colour, pleasant odour, and the consistence of hard butter. It melted in a glass tube drawn out into a capillary opening at about 108°·5 F. It was readily soluble in alcohol and æther; its solution reddened litmus distinctly; it dissolved easily in a cold aqueous solution of potash or a warm solution of carbonate of soda. The latter reaction, and the absence of any acroleine odour when the fat was heated, showed that it was not a glycerine compound, but a free acid, which was further confirmed by the uniformity of the melting-point before and after treatment with potash.

This occurrence of a free fatty acid in a vegetable organ is probably uncommon. Palm-oil indeed always contains free palmitic acid, but this may be owing to a partial decomposition. Heintz has recently furnished a corroboration of this opinion by his observation, that margaric, palmitic, and anthropic acids were formed in human fat which had been kept about half a year. Still Eichhorn regards such a formation of free acid in potato-fat during its preparation as improbable.

In consequence of the ready solubility of this fat in alcohol, spontaneous evaporation left only a warty mass, presenting no signs of crystallization. Microscopic lamellar crystals were however formed from a solution in warm dilute alcohol.

The small quantity of substance did not admit of any examination

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beyond the per-centage composition. Burnt with oxide of copper and oxygen, 100 parts gave—

	I.	II.	III.	IV.
Carbon	74·98	74·53	75·79	75·74
Hydrogen	11·66	11·60	11·47	11·62
Oxygen.....	13·34	13·87	12·74	12·64

The numbers I. and II. were obtained from the fat prepared as above; II. was analysed fourteen days after I.; the numbers III. and IV. were obtained from substance prepared as quickly as possible (two days), because the fat altered rapidly when exposed to the air, as may be observed by comparing II. with the other analyses. The following analyses show this alteration still more distinctly:—

	V.	VI.	VII.	VIII.	IX.
Carbon.....	73·06	73·60	73·05	70·60	70·54
Hydrogen....	11·56	11·48	11·23	11·75	10·80
Oxygen	15·38	14·92	15·72	18·65	18·66

The substance for which the numbers V., VI., and VII. were obtained was the same as I. and II., but had been exposed to the air for eight weeks in a capsule covered with paper. The fat, exposed for a long time to the influence of oxygen and moisture, gave the numbers VIII. and IX. This oxidation was evidently attributable to a liquid acid in the fat, either identical or analogous with oleic acid, as Eichhorn afterwards found.

It will be seen, that when the above analyses, both of the fresh and of the oxidized fat, are expressed in the smallest atomic weights, that the carbon and hydrogen are not in the same proportion as in other fatty acids. They all give a greater number of equivalents of carbon than of hydrogen, the respective mean of the analyses of the fresh fat corresponding to $C^{32} H^{29} O^{4}$, of the fat altered by the air to $C^{31} H^{30} O^{5}$, and of the fat altered by oxygen to $C^{35} H^{32} O^{7}$. This preponderance of carbon equivalents, as in the glycerine compounds of the fatty acids, would certainly have admitted the conjecture that glycerine existed in the potato-fat, were it not for the reaction with carbonate of soda, and the possibility that it may be owing to the presence of an acid analogous to the oleic, which, as well as the rapid oxidation, would cause this inequality in the number of equivalents of carbon and hydrogen. A subsequent determination of the atomic weight of the fat did not show this inequality, as may be seen by the following analyses of the silver salt, prepared with the acids V., VI. and VII.; however, they had been kept for some months, and not particularly protected from the air:—

	X.	XI.		
Carbon	52·89	..	36	53·07
Hydrogen	8·79	8·60	35	8·69
Oxygen	9·22	..	5	9·71
Oxide of silver	29·00	28·02	1	28·55

Consequently the formula $C^{36} H^{35} O^{5} + AgO$ would best express the composition of the silver salt. The determination of this atomic weight, in order to decide whether the fatty acids of potatoes had

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the formula $C^n H^n O^4$, was the more desirable, as the solid fat mentioned at p. 463 differed in its composition from the other fats.

The distilled fat, like the saponified fat, presented the same equality in the number of equivalents of carbon and hydrogen; it gave on analysis in 100 parts—

	XIV.	XV.		
Carbon	73·79	74·63	30	74·38
Hydrogen	12·52	13·09	30	12·40
Oxygen	13·69	12·28	4	13·22

These results not being very satisfactory, another quantity of fat was prepared in the same way from another kind of potato. The product was not larger, its characters were precisely the same, and a minute quantity of the wax-like body was obtained as before. It was saponified, separated by hydrochloric acid, and remelted in water. To obtain it crystallized, it was treated with weak alcohol at a temperature below its melting-point; water was then added until the liquid became turbid; a few drops of alcohol, added while raising the temperature to 104° F., rendered it again clear. Upon cooling the acid crystallized, the whole mass appearing as if solid. When purified by recrystallization, it was quite white. Its melting-point was 125°·6 F.

Eichhorn then treated the fat according to Heintz's process, and succeeded in separating it into two solid fatty acids, whose respective melting-points were 122° and 136°·4 F. The lead salt of the former crystallized in very delicate laminæ upon the cooling of the alcoholic solution of the fat mixed with basic acetate of lead; the lead salt of the latter was obtained from the mother-liquor by precipitating with an excess of basic acetate. When decomposed by hydrochloric acid, both salts yielded white crystalline acids. Their quantity was too small for a repeated treatment with basic acetate. The analysis of the silver salt of the more fusible acid gave in 100 parts—

	XVI.	XVII.	XVIII.	Mean.		
Carbon.....	51·05	..	..	..	51·05	30	51·58
Hydrogen	8·86	..	..	..	8·86	29	8·31
Oxygen	..	..	..	..	6·98	3	6·87
Oxide of silver..	..	33·35	32·87	33·11	33·11	1	33·24

Assuming that in the salts 1 equiv. water is replaced by 1 equiv. of base, the free acid would have the formula $C^{30} H^{30} O^4$. The distilled fat has the same composition, but Eichhorn is undecided as to their identity.

The name proposed for the acid having the formula $C^{30} H^{30} O^4$ is *solano-stearic*. If its composition is really that which Eichhorn supposes, it will fill up an essential gap in the series of acids $C^n H^n O^4$. He was unable to study its chemical behaviour, and mentions no other physical characters but the melting-point, 122° F., and feeble tendency to crystallize, to which must be added volatility if the distilled acid is identical with it.

Basic acetate of lead, added in excess to the mother-liquor remaining after the crystallization of the fat from weak alcohol, threw

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down a slight precipitate, after the removal of which hydrochloric acid separated a brown, viscous, fatty acid, whose baryta salt was soluble in alcohol, and whose alcoholic solution gave no precipitate with acetate of lead. The acid was not analysed, but these characters show that it is not ordinary oleic acid. Eichhorn calls it solanoleic acid.

The general results to which he has arrived are, that the quantity of fat is not uniform for the whole tuber, the peelings containing the largest per-centage;

That this fat consists of three free fatty acids, two solid and one liquid (the latter being probably the cause of the rapid oxidation), and a crystallizable wax, having the composition $C^{36} H^{30} O^{7}$. The fluid fat exists in larger proportion in the peel than in the interior.

With regard to the possible formation of fusel oil, especially oxide of amyle, from acids having the formula $C^{n} H^{n} O^{4}$, Eichhorn points out that the compounds of this body with fatty acids are metameric with the fatty acids higher in the series, thus:—

Acetate of amyle	$C^{14} H^{14} O^{4}$ = œnanthylic acid.
Butyrate of amyle	$C^{18} H^{18} O^{4}$ = pelargonic acid.
Œnanthylate of amyle ..	$C^{24} H^{24} O^{4}$ = laurinic acid.
Caprate of amyle	$C^{30} H^{30} O^{4}$ = solanostearic acid.
Laurinate of amyle.....	$C^{34} H^{34} O^{4}$ = margaric acid.

In order, if possible, to determine whether during fermentation the breaking up of the sugar into alcohol, carbonic acid and water is accompanied by a similar metamorphosis of any fatty acids into amyle compounds of acids lower in the same series, *i. e.* with a smaller hydrocarbon, he fermented two solutions of sugar, one of which contained 2 drms. of potato-fat, dissolved by means of carbonate of soda, to 6 oz. of cane-sugar. The fermentation went on in both liquids alike; no difference of smell could be recognised after its completion, but the liquid containing the fat had a bitter taste, similar to fermented potato-mash. The distillates of the two liquids presented no particular difference. This experiment, though negative, is by no means conclusive. As in other cases, a special ferment may be a necessary condition of the formation of fusel-oil from fat. Such a ferment may be formed from the non-coagulable nitrogenous substances in potato-liquor, and Eichhorn announces his intention of following up the inquiry.—Poggendorff's *Annalen* for October 1852.

On Calluna vulgaris. *By* Fr. Rochleder.

The entire plant, except the root, was cut up and exhausted with alcohol. The dark green fluid was submitted to distillation on the water-bath to remove the alcohol, the residue mixed with water and filtered. There remained upon the filter a green mass, consisting of wax, fat and chlorophylle; the filtered fluid was yellow, and contained principally a peculiar tannic acid, striking a green colour with salts of peroxide of iron, which the author calls *callutannic acid.*

Callutannic acid, $C^{14} H^{6} O^{8}$.—Solution of acetate of lead, added

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to the above-mentioned yellow fluid, gives a dingy yellow precipitate, which is collected on a filter and washed with water. It is then put into a beaker, and dilute acetic acid poured over it. A part of the precipitate dissolves with a yellow colour, whilst another portion remains undissolved, and of a yellowish colour with a brownish-green tinge. The solution is filtered off, and a slight excess of basic acetate of lead added to it whilst boiling. A voluminous precipitate of the colour of chromate of lead is formed, which does not change its appearance when exposed to the air either at ordinary temperatures or at 212° F. Two lead salts, prepared at different times, were analysed, dried at 212° F. The first gave—

Carbon	19·01	28 =	168·00	19·18
Hydrogen	1·68	13	13·00	1·48
Oxygen	15·37	17	136·00	15·54
Oxide of lead	63·94	5	558·69	63·80

$C^{28}H^{13}O^{17}, 5PbO = 2(C^{14}H^{6}O^{8}, 2PbO) + PbO, HO.$

The second gave—

Carbon	18·22	42 =	252·000	18·34
Hydrogen	1·55	20	20·000	1·45
Oxygen	15·06	26	208·000	15·15
Oxide of lead.....	65·17	8	893·904	65·06

$C^{42}H^{20}O^{26}, 8PbO = 3(C^{14}H^{6}O^{8}, 2PbO) + 2(PbO, HO).$

The composition of anhydrous callutannic acid is therefore expressed by the formula $C^{14}H^{6}O^{8}$.

If a lead salt, thus prepared, be diffused in water, and decomposed by sulphuretted hydrogen gas, the fluid heated to boiling with the sulphuret of lead and filtered whilst boiling, a golden-yellow solution of pure callutannic acid is obtained. If this solution be placed in a retort in a chloride of calcium bath, and the water evaporated in a current of carbonic acid gas, the hydrate of callutannic acid remains, which when powdered presents an inodorous mass of an amber-yellow colour. To remove the moisture which had been attracted by the acid during trituration, it was dried *in vacuo* over sulphuric acid. Analysis gave—

Carbon	51·69	14 =	84	51·53
Hydrogen	4·58	7	7	4·30
Oxygen	43·73	9	72	44·17

A solution of chloride of tin, added to a warm watery solution of callutannic acid, gives a fine yellow precipitate, which dissolves in an excess of the precipitant. The composition of this precipitate, dried at 212° F., was—

Carbon	19·20	28 =	168	19·33
Hydrogen.....	2·37	16	16	1·84
Oxygen.....	18·40	20	160	18·42
Peroxide of tin.....	60·03	7	525	60·41

$C^{28}H^{16}O^{20}, 7SnO^{2} = [2(C^{14}H^{6}O^{8})3SnO^{2}] + 4(SnO^{2}, HO).$

The salt contains a slight excess of acid, apparently in consequence of incipient decomposition during the washing.

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With alkalies and alkaline earths, and also with oxide of silver, no compound of callutannic acid could be produced, the first salts becoming rapidly oxidized, but the oxide of silver being reduced.

In its aqueous solution, callutannic acid undergoes a change by the action of mineral acids, particularly when assisted by heat; it loses water, or the elements of water, and is converted into an amorphous yellow or reddish-yellow colouring matter, which is soluble in hot water, but nearly insoluble in cold. The author calls this substance *calluxanthine*. Its preparation succeeds best when concentrated sulphuric acid is added in drops to a concentrated solution of callutannic acid. The liquid acquires a reddish-yellow colour, whilst it becomes heated and slightly turbid. On cooling, yellow flakes are separated, from which the fluid portion, to which some water has been added, is filtered. The calluxanthine is washed with cold water. It is soluble in alcohol. Its solution in alkaline fluids attracts oxygen rapidly; on the addition of acids, a product of oxidation is thrown down in reddish-brown flakes from the dark-coloured fluid. The analysis of the substance, dried at 212° F., gave—

Carbon	58·07	14 =	84	57·93
Hydrogen	3·77	5	5	3·45
Oxygen	38·16	7	56	38·62

The formula $C^{14} H^5 O^7 = C^{14} H^7 O^9 - 2HO$ shows the removal of 2 equivs. of water from the hydrate of the acid.

Callutannic acid in its unchanged condition is a colouring substance, by the employment of which fine yellow colours may be produced. A watery solution of the acid heated to boiling with the addition of chloride of tin and a few drops of muriatic acid, dyed woollen stuffs, prepared with an alum mordant, of various shades of yellow, varying, according to its concentration and the longer or shorter time during which the stuffs were left in contact with the fluid, from pale sulphur-yellow to chrome-yellow or orange. By boiling the dyed stuffs with soap and water, the colour became more lively.

If the twigs and leaves of the *Calluna* be extracted with water instead of alcohol, a brown decoction of a thicker and more slimy nature is obtained, whilst traces of a volatile oil are given off. The slimy nature of the decoction is caused by a substance which, from all its properties, must be considered to belong to the pectine group.

Another acid occurs in the *Calluna vulgaris*, which the author supposes may be citric acid. The decoction also contains a very small quantity of a substance to which he gives the name of *ericoline*.—*Sitzungsber. der Akad. der Wiss. zu Wien*, July 1852.

Note on Camphomethylic Acid. *By* A. Loir.

To obtain camphomethylic acid, I have followed the process indicated by M. Malaguti for the preparation of camphovinic acid, merely substituting methylic for ordinary alcohol.

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This acid presents itself sometimes in the form of needles of several centimetres in length, radiating from a centre, sometimes in that of small hexagonal or quadrilateral plates. Dissolved in æther and evaporated very slowly, it gives very large and distinctly formed isolated crystals, the form of which is a right rhombic prism; the lateral faces forming the acute angle are tangentially modified. The quadrilateral prisms, which are deposited by a very rapid evaporation of the ætherial solution, are a hemihedral modification of this; at each extremity two of the facets forming a cross are developed, so that each pair intersect. These laminæ offer a cleavage parallel to the axis of the prism and perpendicular to the tangential modification; they then reproduce the hexagonal plates.

Camphomethylic acid, dissolved in alcohol, æther or chloroform, acts upon polarized light; it causes the plane of polarization to deviate to the right. The rotatory molecular power of this acid, dissolved in alcohol of 95°, is 51°·4 for a thickness of 100 millims. for the yellow rays.

Camphomethylic acid crystallizes very readily from its solutions in alcohol, æther and chloroform; it is but slightly soluble in water; its alcoholic solution reddens litmus strongly. It melts at a temperature of 152° F. At a more elevated temperature, it gives anhydrous camphoric acid, a viscous liquid, and a small residuum of carbon.

When well-dried crystals of this acid are heated with a solution of potash, the products of distillation received in a freezing mixture present the properties of wood-spirit (odour, inflammability, &c.); camphorate of potash remains in the retort. The crystals of this acid, placed over sulphuric acid in a bell-glass, do not lose in weight. Its composition is—

	Found.	Calculated ($C^{22}H^{18}O^{8}$).
Carbon	61·37	61·60
Hydrogen	8·48	8·41
Oxygen	30·15	29·99

Comptes Rendus, Sept. 6, 1852, p. 328.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Composition of the Substances employed by the Chinese in the Decoration of Porcelain. *By* MM. Ebelmen *and* Salvétat.

[Concluded from page 457.]

6. *Reds.*

It has already been stated, that the substance called *fan-hong*, contained both in the collection of the Musée Céramique and in that of the Ecole des Mines, although classed amongst the reds, was not

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a colour, but only an oxide of iron serving as a base to several colours. The authors have found that four colours in M. Itier's collection contained this substance. Three of these were nothing but *fan-hong* mixed with a substance, the object of which is to fix and glaze the oxide of iron; to these M. Itier has given the names of *jaune orangé rouille, couleur de chair* and *couleur de rouille.* The fourth is a mixture of one of the preceding with the yellow *chang-hoang*; this is called *jaune sale* by M. Itier.

Ta-hong, i. e. strong red (ticketed *jaune orangé rouille*).—This is in elongated, amorphous, rounded, shining fragments, not friable, crushed with difficulty, and burning with a very distinct odour of glue. In the fire it loses 24·4 per cent. of its weight; with dilute nitric acid it gives a prolonged effervescence, and the fluid contains an abundance of lead. Boiling muriatic acid destroys its colour completely. All these characters show that this colour consists of a mixture of white lead (*yuen-feng*) with oxide of iron (*fan-hong*) and glue.

This colour, laid upon porcelain, and exposed to a heat at which other colours become sufficiently glazed, became adherent only in the thin parts; the thicker portions remained pulverulent.

Tse-hong, or fine rose-red (ticketed *couleur de chair*).—This colour is in bright red fragments, of a more rosy tint than those constituting the *ta-hong.* It is difficult to powder; and when calcined, exhales the characteristic odour of burnt glue. It effervesces with dilute nitric acid, which afterwards contains lead; its colour is destroyed by boiling muriatic acid; it contains only a small percentage of silica. When applied to porcelain, it behaves exactly like the preceding red. The analysis of these two reds gives—

	Ta-hong.	Tse-hong.
Loss by heat	24·40	23·40
Silica	0·90	5·60
Oxide of lead	59·00	62·52
Oxide of copper	trace	trace
Alumina and peroxide of iron	14·15	7·20
Lime	1·00	1·00
Magnesia	trace	trace
Loss	0·55	0·28

Silica is wanting in both these colours, the small quantity found in the second arising probably from the addition of a little flux. This colouring oxide is not the only one which can be transformed into a porcelain colour by the simple addition of oxide of lead, as we have seen in analysing the Chinese porcelain-blacks. This mode of employment, from the want of siliceous flux, sufficiently explains why the colours only burn smooth in the thinner portions, remaining dull and powdery when laid on thicker.

These analyses confirm the statements of Father Ly with regard to *fan-hong*, in the descriptive catalogue of the collection of the Ecole des Mines:—"To every ounce 5 oz. of white lead are added, and the whole triturated together; the mixture thus formed is used

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as a colour." In M. Itier's first red the oxides of lead and iron exist in the same proportions.

P'ao-chi-hong, i. e. precious stone-red (ticketed *couleur de rouille*).—This colour differs completely from the preceding in the manner in which it behaves in the fire, glazing both in the thick and thin parts. It is with this colour that the Chinese produce those shining red grounds, in the midst of which they frequently form, by scraping, white ornaments with the happiest effect.

It is a homogeneous red powder, emitting no odour of burnt glue when calcined. It effervesces only for a very short time with dilute nitric acid; the solution gives a black precipitate with sulphuretted hydrogen. The colour is destroyed by boiling muriatic acid. The solution behaves like a solution of iron in nitromuriatic acid containing a little chloride of lead. Analysis:—

Loss by heat	2·20
Silica	36·10
Oxide of lead	41·16
Oxide of copper	trace
Oxide of iron and alumina	17·00
Magnesia	trace
Lime	1·10
Alkalies and loss	2·44

Kou-tong, i. e. old copper or old bronze (ticketed *jaune sale*).—This is a brick-red powder, which when burnt on porcelain gives only a dull yellow tint, without glazing; this is the behaviour of a mixture of a yellow with an iron-red. The colour therefore does not possess the tint which it exhibits after burning. Boiling muriatic acid destroys all its colour; the resulting liquid contains antimony, lead and iron. Analysis:—

Loss by heat	6·80
Silica	22·00
Oxide of lead	56·64
Oxide of copper	0·20
Oxide of iron	7·20
Alumina	0·40
Lime	1·40
Magnesia	trace
Antimonic acid	1·02
Alkalies and loss	4·34

From this it appears that the Chinese understand the use of oxide of iron to produce both glazed and unglazed red colours, but it is remarkable that they should be ignorant of the different tints which may be obtained with this same substance, by exposing it during its preparation to a gradually elevated temperature.

Other Chinese reds, obtained by the authors from M. Itier's and Father Ly's collection, and from that of the Musée Céramique, are the following:—

Seng-yen-tchy-hong, or red of first quality, requiring no addition;

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for use it must be pounded (Ly).—This consists of brownish, lustrous fragments, externally vitrified, and presenting internally some pulverulent rose-coloured portions. The external fragments give a rose-coloured powder with a slight violet tint. This powder is the same as the

Si-yen-tchy-hong, or prepared red of first quality, used without addition of *yuen-feng* (Ly).—It contains some carbonate of lead. These two colours have the strongest affinity with the two following.

Seng-ting-hong, *i. e.* red of second quality, requiring no addition of *yuen-feng*; for use it must be pounded (Ly).

Si-ting-hong, prepared red of second quality, requiring no addition of *yuen-feng* (Ly).—These colours are attacked with difficulty by cold nitric, muriatic and nitromuriatic acids. Hot concentrated nitric acid takes up a large quantity of oxide of lead and some silica, but part of this remains in a gelatinous state. The rose colour is persistent, and seems to become concentrated in the residue insoluble in nitric acid. This residue is rapidly attacked by hot concentrated solutions of potash and soda, or their carbonates, leaving only a few blue flakes of finely-divided gold. Boiling nitromuriatic acid destroys this colour; there remains a deposit of silica and chloride of lead; the colour disappears, and the liquid contains perchloride of gold. Boiling muriatic acid dissolves it with difficulty, and leaves an unattacked powder; the liquid does not contain any gold. The colour contains neither tin nor boracic acid; its essential constituents are silica, oxide of lead, potash, soda and gold; its inessential constituents, alumina, copper, iron, lime and magnesia. The analysis of the two colours in both states gives the following results:—

	Yen-tchy-hong.		Ting-hong.	
	Seng.	Si.	Seng.	Si.
Loss by heat	1·21	3·60	1·19	3·20
Silica	40·00	38·80	39·71	38·30
Oxide of lead	48·55	47·37	48·70	48·00
Alumina	0·20	trace	0·45	0·29
Peroxide of iron	0·31	0·30	0·23	0·30
Lime	trace	trace	0·41	0·15
Magnesia	0·05	trace	trace	trace
Potash and soda	8·00	7·54	7·90	7·60
Oxide of copper	0·40	0·40	0·30	0·44
Metallic gold	0·20	0·25	0·20	0·30
Loss	1·08	1·74	0·91	1·42

The quantity of gold was determined in the dry way by fusing 10 grms. of the colour with 15 grms. of tartrate of soda, 10 of borax, and 10 of fused carbonate of soda; the mixture was allowed to cool in the crucible, which was then broken, and the gold obtained by cupellation from the button of lead formed; the gold weighed 0·025 grm., which agrees with the quantity ascertained by the humid way.

From these analyses it appears that these four colours are identical. They came from King-te-tching; a sample of the following colour, obtained by M. Itier at Canton, having the same composi-

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tion, we may regard it as the general constitution of gold colours in China.

Hong-hoa, i. e. safflower-red (ticketed *laque rose sale*).—It is a rose-coloured powder, slightly purple, which behaves with acids like the preceding colours. It is, in fact, the same substance, as may be seen from the analysis:—

Loss by heat	1·40
Silica	41·78
Oxide of lead	44·13
Oxide of copper	0·26
Alumina and oxide of iron	2·40
Lime	1·60
Magnesia	0·11
Metallic gold	0·38
Alkalies and loss	7·94

M. Itier's collection contains two more colours, consisting of mixtures of this red with other colours which have already been noticed.

Tsing-lien, i. e. nenuphar-blue (ticketed *amaranthe foncé*).—A light violet powder, which under water is seen to consist of three differently-coloured substances,—one colourless, the second rose-colour, the third blue. The mixture effervesces very slightly with dilute nitric acid.

Hong-fen, or red powder, literally red meal (ticketed *rose couleur cobalt*).—A pale rose-coloured powder, consisting of a mixture of white and red powders. The authors have not been able to find the least trace of oxide of cobalt. The analysis of these two colours gave—

	Tsing-lien.	Hong-fen.
Loss by fire	2·00	1·40
Silica and oxide of tin	41·80	39·30
Oxide of lead	45·16	48·25
Oxide of copper	0·50	0·20
Alumina and oxide of iron	0·60	1·00
Lime	1·20	2·02
Magnesia	trace	0·05
Metallic gold	0·20	0·35
Oxide of cobalt	0·20	0·00
Undetermined substances	8·34	7·43

Thus, whatever be the source of the Chinese porcelain colours, they all present a very striking general character,—a slightly varying glass, composed of silica, oxide of lead, soda and potash, containing as silicates a certain per-centage of colouring oxide. The only exceptions are the oxides of iron and manganese, employed as reds and blacks; and this is the case only because these oxides, if dissolved in silica, no longer furnish red and black colours. No colour contains borax or boracic acid. This peculiarity in the composition of the Chinese colours naturally induces peculiarities in the decorations which they are employed to produce, and thus it is that the Chinese and Japanese porcelain paintings acquire their distinctive character.

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The multiplicity of colours produced in Europe by mixture is unknown to the Chinese, and they are even quite ignorant of many of our materials. Their colouring matters are limited to oxide of copper, gold, antimony, arsenic, tin, impure oxide of cobalt, oxide of iron and oxide of manganese. In Europe, when they make use of these various oxides, they derive great advantage from substances unknown to the Chinese. Thus the tint of pure oxide of cobalt is modified by the addition of oxide of zinc or alumina, or sometimes of alumina and oxide of chromium; pure oxide of iron furnishes about ten reds; by combining different proportions of oxide of iron, oxide of zinc, and oxide of cobalt or nickel, pale and dark ochres are obtained; browns are prepared by increasing the quantity of cobalt in the composition of the ochre, and blacks by the suppression of the oxide of zinc, in the same preparations. Yellows are rendered paler by the addition of oxide of zinc or tin, darker by oxide of iron. Oxide of chromium, either pure or combined with oxide of cobalt, or with the oxides of cobalt and zinc, gives a series of greens, varying from yellowish-green almost to pure blue. Metallic gold furnishes the purple of Cassius, which may be transformed at will into violet, purple or carmine. Oxide of uranium, and the chromates of iron, cadmium and baryta, furnish useful colours; and lastly, we employ the metals which are inoxidable in the fire, and the preparation of which requires a degree of chemical knowledge which the Chinese are far from possessing.

All these oxides are simply mixed in the European colours, whilst in the Chinese they are dissolved. In fact, the following analyses of materials known in France as enamels exhibit exactly the same composition as the Chinese porcelain colours. These are enamels used for articles of bijouterie in copper, gold and silver:—

	Blue for copper.	Gold for copper.	Green for silver.
Loss by heat	1·00	0·06	0·10
Silica	51·00	47·70	53·68
Oxide of lead	34·57	31·19	25·30
Oxide of cobalt	1·00	0·10	0·00
Oxide of iron	trace	0·40	0·46
Oxide of manganese	0·00	1·20	0·20
Alumina	trace	0·26	0·60
Lime	2·00	1·80	1·26
Magnesia	trace	trace	trace
Oxide of copper	trace	trace	0·60
Metallic gold	..	0·46	0·00
Potash and soda	10·43	13·23	17·80
Oxide of tin	..	3·60	0·00

The fluxes which are used in enamelling on gold, silver and copper, and that which is applied over the painting called *sous-fondant* in France, may also be compared with the colours used by the Chinese in the decoration of their porcelains; it will be seen that these compounds are similar. The only difference is in the degree of fusibility, which is greater in the Chinese enamels:—

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	Flux for silver.	Flux for gold.	Flux for painting (*sous-fondant.*)
Loss by heat	0·30	0·10	0·10
Silica	48·10	53·60	44·82
Oxide of lead.....	38·25	31·19	41·59
Oxide of copper	0·32	trace	trace
Oxide of iron.....	0·25	0·40	0·31
Oxide of manganese ..	0·00	0·60	0·15
Alumina.....	0·14	0·54	0·46
Lime	0·60	1·26	0·82
Magnesia	trace	trace	0·05
Alkalies.....	12·04	12·31	11·70

The similarity exhibited by the comparison of the composition of these enamels with the Chinese porcelain colours, is also shown in the behaviour of both in the fire on porcelain. It has long been known that enamels will not burn on European porcelains, from their scaling off. The Chinese colours sent by Father Ly and M. Itier, when tried upon European porcelain at Sèvres, acted in exactly the same manner, whilst when applied to Chinese porcelain they burnt well in. The authors consider that the cause of this lies in the difference between the glaze of the two porcelains. It is stated in the former part of this paper, that the Chinese porcelain mass, being more fusible than the European, must therefore be covered with a more fusible glaze; and it is the introduction of lime into the glaze, which, diminishing its infusibility and modifying perhaps its dilatability, approximates its physical properties to those of enamels.

If the aspect of the Chinese porcelains be different from that of the European, if the harmony of their decorations appears more varied, it is, according to the authors, the necessary result of their methods. All their colours contain but little colouring matter; they only possess strength of tone when laid on to a thickness which gives their paintings a relief which it is impossible to obtain by other means; the harmony of their paintings is the consequence of the nature and composition of their enamels.

In addition to samples of the colours used in China, Father Ly has also sent specimens of the gold employed there in the decoration of porcelain, of the substance used as a diluent, and of the pencils employed in laying on the colours.

Metal.

Gold is the only metal used by the Chinese. Father Ly has sent two specimens, the one green, the other yellow gold.

Khong-tchhy-king is prepared gold colour of the first quality.

Koang-king, prepared gold colour of second quality.

The samples resemble that known in Europe as *honey-gold* or *shell-gold*. According to Father d'Entrecolles, the gold is powdered and laid on the wet surface of a porcelain vessel until a thin layer of gold is formed. It is then dried; for use, it is diffused in a sufficient quantity of gum-water, and 3 parts of white lead mixed with

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every 30 parts of gold. It is curious that the proportion of gold and flux employed is the same as at Sèvres; the flux employed at that place, instead of white lead, is the basic nitrate of bismuth.

Diluents.

The Chinese use water to dilute their colours, instead of oil of turpentine, which is employed for this purpose in Europe. Only a few colours require the addition of a particular substance to render their employment easy. This substance is called *yeou-p'ky-hao*; it is a size made of bullock's skin. The colours to which it is added are, according to Father Ly, *fan-hong*, *feng-hong* and *ching-lan*; but the authors have also found it in the black called *si-feng-liao* by M. Itier. It is this substance which produces the odour of burnt glue evolved by these colours on calcination.

Pencils.

M. Itier brought from Canton an assortment of the pencils with which the Chinese of that place applied their colours to porcelain. The collection of the Ecole des Mines contains an assortment sent from King-te-ching by Father Ly. All these pencils are of a similar structure; they consist of a long hollow stalk, like a reed, in the interior and at the extremity of which some very long hairs are firmly fixed. According to Father Ly, "there are common and fine brushes: some serve for laying on various colours, others for painting delicate flowers, some for painting with common red, others with fine red."

Summary.

This examination of the materials employed by the Chinese in the decoration of porcelain leads to the following results:—

1. The *muffle colours*, that is to say colours which bake at a very low temperature compared with that necessary for the baking of the porcelain, are far less numerous.

2. The palette is not composed of colours properly so called, but of *enamels*; that is to say, of plumbo-alkaline glasses, variously coloured by means of a small per-centage of *dissolved* colouring oxides.

3. The composition of the glass is in general but little varied, and the coloration always slight: it is this lightness of tone, together with the liveliness of the tint, which gives the Chinese porcelains their characteristic harmony and richness.

4. The enamels are coloured by oxide of cobalt, oxide of copper, gold, antimony, tin and arsenic.

5. The enamels are applied with water, sometimes with the addition of some size formed of bullock's skin.

There are also certain hard colouring matters employed by the Chinese in various ways, of which the authors have said nothing in their present memoir; they propose to make them the subject of a third and last memoir on this subject.—*Ann. de Chim. et de Phys.*, July 1852, pp. 332–365.

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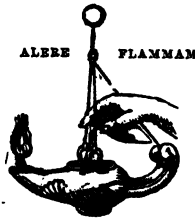

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